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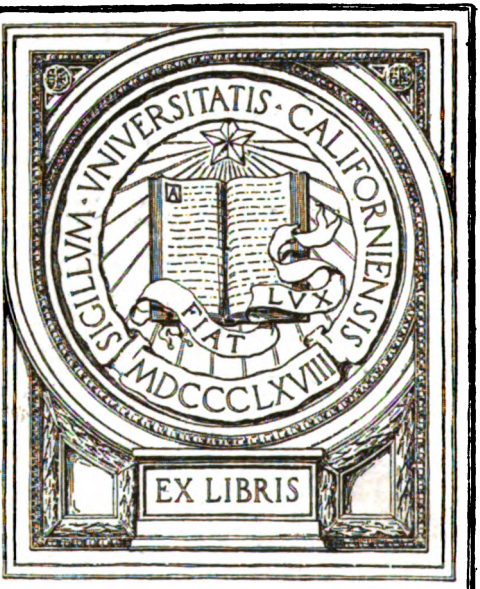

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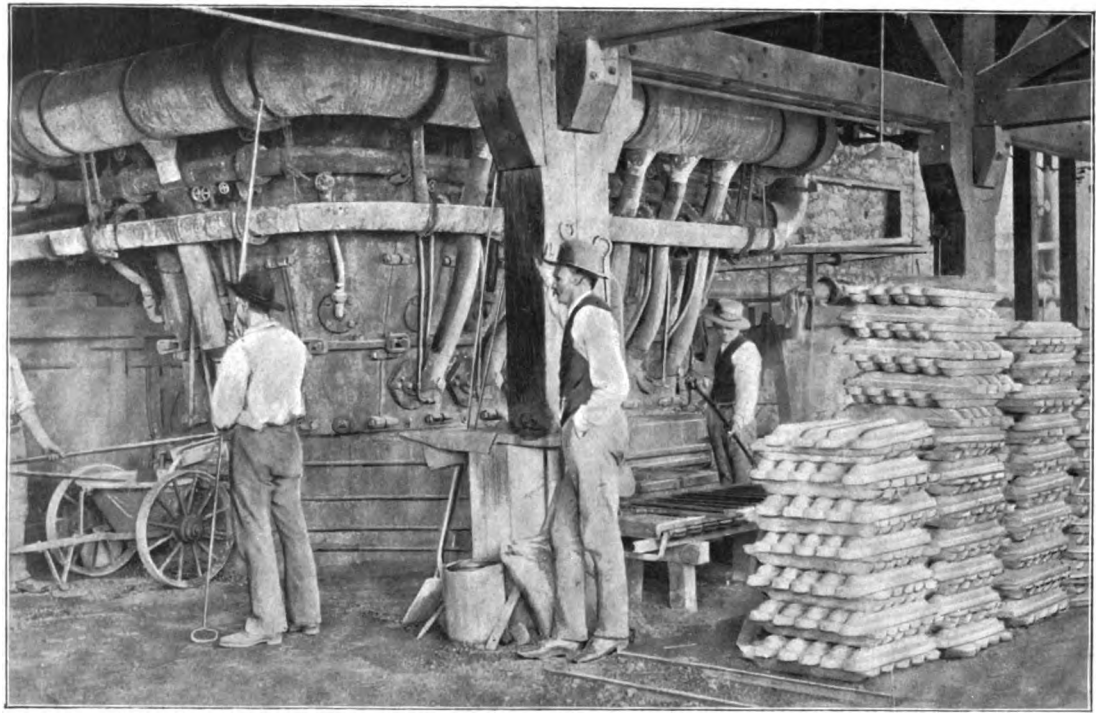

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BY

HENRY F. COLLINS,

ASSOCIATE ROYAL SCHOOL OF MINES,
ASSOCIATE-MEMBER OF THE INSTITUTION OF CIVIL ENGINEERS, MEMBER OF THE INSTITUTION OF MINING AND METALLURGY, MEMBER OF THE AMERICAN INSTITUTE OF MINING ENGINEERS, OF THE MINERALOGICAL SOCIETY OF GREAT BRITAIN AND IRELAND, ETC.

PART I.—LEAD.

Being one of a Series of Treatises on Metallurgy written by Associates of the Royal School of Mines.

EDITED BY

SIR W. C. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S.

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Dedication.

TO MY FATHER,

J. H. COLLINS, F.G.S.,

PAST-PRESIDENT OF THE INSTITUTION OF MINING AND METALLURGY,

&c., &c., &c.,

I am indebted for an early training in those branches of Natural and Applied Science, of which he himself has been an earnest student and an accomplished teacher. For this early training I can never be sufficiently grateful, and to it must in justice be attributed such measure of success as I may hereafter achieve. To my father, therefore, this book is (without permission) dedicated by

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PREFACE.

THE object of Part I. of this treatise is to supply a condensed compendium of information on the Metallurgy of Lead, accurate as well as fairly up-to-date, and useful, therefore, to the busy working metallurgist as well as to the student. As regards American and German practice, the ground has been so well covered by the recent works of Hofman and Schnabel, that little has been attempted beyond condensing the information contained in the above works, supplementing it from other contemporary sources and from the Author's own practical experience and observation, and presenting a digest of the whole in a compact form.

In addition, however, Australian practice in smelting and in desilverisation will be found here described for the first time in considerable detail. It is further hoped that the standpoint aimed at in considering the whole subject, which is cosmopolitan rather than one mainly American or German, will render the information supplied more useful to English students and metallurgists.

With the object of economising space, as well as of facilitating reference and comparison, details of the practice at particular localities have been, as far as possible, thrown into the form of tabular statements. These will be found scattered throughout the book in almost every chapter, and it is hoped they will prove a useful feature.

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Free use has been made of published literature on the subject, so far as it has been available to the Author. The source of all contributions is acknowledged in the footnotes, but special acknowledgment should be made to the works of Hofman (*Metallurgy of Lead*, 2nd edition, New York, 1893) and Schnabel (*Handbuch der Metallhüttenkunde*, Berlin, 1894), to the *Engineering and Mining Journal* of New York, the *Transactions of the American Institution of Mining Engineers*, the Columbia College *School of Mines Quarterly*, and the *Berg- und Hüttenmännische Zeitung;* also to those friends who have supplied statistical information, and to many gentlemen in charge of metallurgical works, who, although personally strangers, have very kindly afforded the Author most valuable assistance.

Errors may have crept in, partly owing to the exigencies of a busy professional life, partly through the Author's absence from civilisation, which rendered it impossible for him to read all the proof-sheets. For all such shortcomings, he begs indulgent consideration at the hands of those who may have occasion to read or consult these pages.

HENRY F. COLLINS.

MINA DE STA. FE,
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THE METALLURGY OF LEAD AND SILVER.

PART I.—LEAD.

SECTION I.—INTRODUCTORY.

CHAPTER I.

SAMPLING AND ASSAYING OF LEAD AND SILVER ORES.

Sampling of Ores.*—Ores frequently arrive at a smelting or other metallurgical works in a more or less damp condition; hence the first operation after weighing the parcel or lot is that of taking a sample for moisture. For this purpose several pounds are taken from different parts of the heap or from different sacks, and immediately carried in a covered can (after roughly crushing, if necessary) to the assay office, where duplicate quantities, of say 2 lbs. each, are weighed out and dried in an iron or porcelain dish.

The sampling proper is, except in the case of very rich silver ores, always begun by the method of *fractional selection*. This consists in setting aside as the bulk sample every fifth, tenth, or, in the case of very poor ores, every twentieth shovelful or sackful as unloaded. This bulk sample, if not already broken at least to egg-size, must be passed through a crusher before the next operation can be undertaken. Its further reduction may be effected by hand or machine. The former method is commoner

* The student may consult with advantage Reed, *S.M.Q.*, vol. iii., p. 253; vol. vi., p. 351; Glenn, *Trans. A.I.M.E.*, vol. xx., p. 155; Johnson, *E.M.J.*, 1892, Jan. 16 and 23; also Hofman, *Metallurgy of Lead*, N.Y., 1893, pp. 45-68, where American methods are given in detail.

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in Europe, and wherever labour is cheap; the latter method, requiring less labour, and occupying much less space, besides being more exempt from any suspicion of unfairness, is coming into use throughout the United States. Mechanical sampling has, however, three grave defects:—(1) The process is not open to view all the time; (2) the working parts of the machines are comparatively difficult to get at and thoroughly clean between successive samplings. This is a serious objection in a works receiving lots of ore which contain from 10 ozs. up to 1000 ozs. per ton. (3) The whole of the sample to be passed through a machine must be crushed much finer than is necessary in the case of hand sampling. This is an objection from the point of view of the blast furnace smelter, as regards such of his ores as do not require roasting; it makes no difference, however, in the case of ores which are to be roasted or milled.

Mechanical Sampling.—Sampling machines are constructed on two different principles. In the first, or "*continuous*," kind a certain proportion (often one half) of the stream of ore falling from a funnel is continuously diverted to one side, the same process being repeated at a lower level on the remainder of the stream until what is left, say one-eighth or one-sixteenth, is sufficiently small to serve as the bulk sample. On this principle is the *Pipe Ore Sampler* supplied by Messrs. Fraser & Chalmers,* but the great objection to all in this class of machine is that a falling stream of ore is by no means uniform over all parts of its sectional area, and therefore the sample resulting *may* not correctly represent the bulk run through the machine.

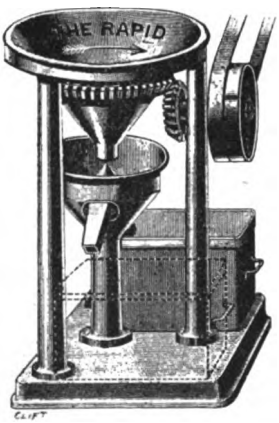

Fig. 1.—Clarkson's Ore Sampler.

An English machine of this class, though on an improved principle, is that of *Clarkson*, which consists of a revolving conical hopper, which, by means of a fixed cone placed beneath, spreads the material to be sampled in the form of a rotating annular stream. Two equal segmental spouts collect two similar and independent samples, which may be made at pleasure, 5 per cent. or 10 per cent. each of the original material. Fig. 1† shows the construction of this machine, which must be regarded as a great improvement on all others of its class.

* Figured in Hofman, *op. cit.*, p. 53.
† Taken from Foster, *Ore and Stone Mining*, p. 635.

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In the second, or *intermittent*, kind of sampling machine, the whole stream of ore is deflected for a certain fraction of time, say one-fourth or one-eighth of a revolution, and this same intermittent deflection is continued till a fraction of manageable size is obtained, which, if the stream has been fairly steady, will be a true sample of the whole. Two good machines of this class are those of *Brunton* * and *Bridgman* †; the latter, like Clarkson's, can take simultaneously two perfectly independent duplicate samples.

Hand Sampling.—Instead of requiring all the parcel of ore to be crushed moderately fine at once, the system of hand sampling admits of a gradual reduction in size by stages of only the portion selected at each preceding stage, the rejected bulk of the ore thus remaining much coarser than is necessary for accurate work in machine sampling. As pointed out by Reed ‡ for ores of any given grade, there is a definite maximum ratio between the bulk of the sample which is to be reduced in size at each stage and that of the largest individual piece; and where accurate results are required from hand sampling this ratio must be clearly borne in mind. The following table slightly modified from Reed shows approximately the maximum size permissible before commencing each successive stage in the reduction :—

Bulk at Each Stage. Reduction from—	Value in Silver—Oz. per Ton.		
	Richest lump, 300 ozs. Average between 20 and 50 ozs.	Richest lump, 3000 ozs. Average between 50 and 150 ozs.	Richest lump, 10,000 ozs. Average, say, 500 ozs.
100 tons to 10 tons, .	Cocoanut.	Fist.	Small orange.
10 tons to 1 ton, . .	Orange.	Egg.	Walnut.
1 ton to 200 lbs., .	Walnut.	Filbert.	Filbert.
200 lbs. to 20 lbs., . .	Pea.	Wheat.	Wheat.
20 lbs. to 4 or 5 lbs., .	12 mesh.	16 mesh.	20 mesh.
4 or 5 lbs. to bottle sample	80 mesh.	100 mesh.	120 mesh.

Hand sampling is still largely employed, and even to some extent in the United States§; the chief requisite for carrying it out is a large sampling floor under cover, as level and closely laid

* *Trans. A.I.M.E.*, vol. xiii., p. 639; and Hofman, *op. cit.*, p. 55.
† *Trans. A.I.M.E.*, vol. xx., p. 416; also Hofman, *op. cit.*, p. 58.
‡ *S.M.Q.*, vol. vi., p. 357.
§ See the author's paper in *Proc. Civ. Eng.*, vol. cxii., Part II., p. 141. Brunton in a recent paper read at the Atlanta meeting of the A.I.M.E. (Oct. 1895) ably discusses this question of crushing between different stages of the cutting down, and arrives at certain figures which differ considerably from those given by Reed (*v. Trans. A.I.M.E.*, vol. xxv., pp. 826-844).

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as possible. Frequently a double layer of plank is employed, so as to permit of more easy replacement when worn, but sometimes a single layer of thoroughly well-seasoned oak plank 2 inches thick is found sufficient. A better arrangement is to have, at any rate, that part of the floor intended for quartering down samples of less than a ton in weight made of heavy boiler plates, with planed edges closely butted, and fastened by means of countersunk screws.

Two main methods are employed for "cutting down" a sample —viz., "quartering" and "split-shovelling."

Quartering.—In this operation the ore coming from the crusher- or rolls-shoot is wheeled on to the floor and tipped, so as to form a ring 8 to 16 feet in diameter. Within this ring when completed two samplers stand on opposite sides, and walking round the circle in the same direction, so as to always remain diametrically opposite each other, they throw alternately shovelsful of ore to the centre of the ring. In doing so, care is taken that each shovelful shall fall directly upon the apex of the conical heap already formed, so that it may spread evenly down the sides. When the ring has been transferred to the centre the floor is swept up, the sweepings being placed on the top of the cone. The heap is then cut down by two or four men with square-ended shovels, who walk round it working in pairs on opposite sides, and beginning about two-thirds of the way up, chop it down outwards till it takes the form of a flat circular cake from 6 to 15 feet diameter and from 6 to 12 inches thick. The cake is then cut into four quarters (whence the name "quartering") by means of a straight-edge, or merely by marking its surface and making paths through it with a shovel; two opposite corners are then removed to a bin, where they remain until settlement is made, in case re-sampling should be demanded by the seller. From the remaining two quarters a new cone is built up in another spot a few feet away, and the same process is repeated until the sample is small enough for another crushing operation, which is performed by rolls when the sample is already of nut size or smaller. When the ore is very dry it is advisable to damp it down with a hose, to make the fine dust, which is frequently the richest part, stick properly to the lumps; otherwise a portion of it may be blown away, or become unevenly distributed through the coarse, which would lead to error.

Split-Shovel Method.—The tool known as the split-shovel consists of a narrow deep trough or series of troughs the same length as a square-ended shovel, and attached to a similar handle. The width of the troughs is determined by the maximum size of the particles of ore, and should be four times the diameter of the largest piece, so that ore of ½-inch mesh requires 2-inch troughs. The split-shovel for coarse ore above filbert size

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may be a single trough one-fourth or one-eighth the width of the square-ended delivering shovel; but for finer ore it is preferably composed of several troughs, the aggregate width of which is one-fourth or one-half the width of the delivering shovel. In this method of sampling, two men face each other, the split-shovel being held by the assistant while the sampler throws the ore from his square-ended shovel in a wide flat stream directly towards the troughs. A definite proportion, one-fourth to one-half, is thus caught in the troughs, the remainder passing through to form the rejected heap. When nearly full, the troughs are emptied on to a separate heap, which is the reduced sample. The process is repeated until the sample is small enough to

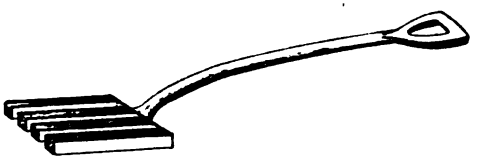

Fig. 2.—Split Shovel.

require crushing finer, when the same process is repeated over another split-shovel with narrower troughs. A split-shovel with four troughs is shown in Fig. 2.

Brunton * has patented a useful tool, which he calls a "quartering-shovel" (Fig. 3), and which greatly lessens the time and labour of cutting down. It works on the split-shovel principle, but saves the labour of one man; it is filled like an ordinary shovel by digging into the heap, the operator then

Fig. 3.—Quartering Shovel.

by a swift backward swing throws out three-fourths of the load over the open back of the shovel into the rejected heap, while the remaining one-fourth retained in the deep central trough forms the sample.

Finishing Sample.—When a sample has been cut down by either of the above methods to about 100 lbs. it is usually passed through a pair of fine rolls which reduce it to about 10 mesh size (or smaller in the case of very rich ores), and is then again quartered or split-shovelled down to about 10 or 20 lbs., which is taken to the "bucking room" for further

* *E. and M. J.*, June 20, 1891.

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reduction. Sometimes this is done by hand, more commonly by a sample grinder of the coffee-mill type; in any case the whole sample is ground to pass a mesh which, on different ores and at different works, varies from 12 to 20 holes to the linear inch. It is then again reduced by quartering, or by the use of the "sampling tin" (which is only a split-shovel on a very small scale) till it weighs only 2 or 3 lbs. This final sample is dried and ground down on a clean bucking plate till it passes an 80 or 100 mesh sieve, and then after thorough mixing by rolling over and over on a sheet of thin indiarubber is filled into bottles or stout paper bags, which are sealed. In every case one sample is given to the works' assayer, one to the seller of the ore or his assayer, and one or more others are retained as "checks" or "controls" in case dispute should arise.

In case part of the sample remains upon the sieve as metallic threads or scales, which frequently happens in the case of ores containing native silver or "chlorides," such portion is weighed and assayed separately, the weight of sample passing the sieve being also determined. The correct assay value of the ore is then the amount shown by assay of the fine powder *plus* the assay of the "metallics" calculated back on the weight of sample which passed the sieve.

Assaying.—This term, strictly speaking, should be confined to the determination of the lead and silver contents as a basis for purchase, and as regards rich galenas little else is ever required. In the case of complex ores, however, it is necessary to determine many other ingredients, not only as a guide in making up the furnace charges, but also as a basis for purchase, as will be afterwards explained (Chap. viii.).

The determination of lead, silver, and gold as a basis for purchase is always made in the dry way—all other constituents are determined in the wet way by short and convenient methods, most of them volumetric. These are described in Chap. viii. on the *Calculation of Charges*.

Dry Assay for Lead.*—There are many different modifications of the dry assay for lead, but only the two which give most satisfactory results need be described here.

1. *Method for Pure Galenas containing upwards of 70 per cent. Lead.*—The best method is the *iron crucible assay*, commonly used in England, and in Belgium and Silesia; it is performed in the ordinary crucible wind-furnace, and the crucible employed is of wrought iron 4 inches high. The quantity of ore taken is usually 400 grains or 30 grammes (at Tarnowitz 50 grammes), and the flux employed is, according to Percy, a mixture of

* The student may consult Phillips' *Elements of Metallurgy*, 1891, pp. 626, *et seq.*; Percy, *Metallurgy of Lead*, pp. 104-119; Balling, *Probirkunde*, Brunswick, 1879, and Gautier's translation, *Manuel de l'art de l'Essayeur*, Paris, 1881; Mitchell's *Manual of Assaying*, &c.

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carbonate of soda 7 parts, dried borax 3 parts, and cream of tartar 1 part,* an equal quantity of which is mixed with the weighed sample. The iron crucible is brought to a bright red heat, the mixture shot in from a copper scoop, and the crucible replaced in a hot fire without loss of time, a "cover" of borax being added. As soon as the mixture is completely melted (which should take about five minutes), the contents of the crucible are stirred and its sides scraped down with a chisel-ended iron rod. The crucible is returned to the furnace for a few minutes, again removed, the sides again scraped down and the stirrer washed in the slag, after which the crucible is tapped a few times to settle the lead, and poured; any small globules adhering to the pot being also turned out by a sharp tap or two of the crucible held upside down in the tongs. When cool, the button of lead is separated from the slag (which is generally quite clean), cleaned, and "cubed up" under the hammer, and weighed. Pure galenas, by this method, will always yield 84 per cent. of lead, provided the temperature is high enough to complete the assay in ten minutes, whereas with the "iron-nail" and other methods it is impossible to get more than 82 or 82½ per cent. Percy proved† that when the gangue consists exclusively of calcite or barytes the results given by this method are not materially lower in the case of even very poor ores than with rich, the actual loss averaging only 1 to 1½ per cent. on the weight of ore taken. When, however, the gangue consists mainly of silica the results on poor ores (8 to 25 per cent.) are from 3 to 3½ per cent. lower than the truth, this error in the case of an 8 per cent. ore amounting to no less than 35 per cent. of the total lead present.

2. *Method for every other Variety of Lead Ore.*‡—Many different methods of assay in clay crucibles have been recommended in works on assaying, and the number of fluxing mixtures employed is very large, but according to pretty general experience no method is so universally applicable as the so-called "Colorado assay," which is practically identical with the Freiberg assay described by Balling,§ and was undoubtedly brought from Freiberg. The assay is conducted in the ordinary large scorification muffle, which is 19 inches by 12 inches inside, and the crucibles used are the "Colorado A A and A" of the Battersea Crucible Company, the former (corresponding with the 5-gramme cup of the Denver Fireclay Co.) being 2½ inches high

* The author has found that ordinary "lead flux," composed as described in the next section, can be advantageously substituted for this mixture.

† *Metallurgy of Lead*, pp. 113, *et seq.*

‡ *v.* Furman, *Manual of Practical Assaying*, N. Y., 1893, p. 137; also Hofman, *Metallurgy of Lead*, N. Y., 1893, p. 70; Iles, *S. M. Q.*, vol. xv., p. 336.

§ French edition, *Manuel de l'art de l'Essayeur*, 1881, p. 444.

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by 2¼ inches wide at top, and the latter 3 inches high by 2¾ inches wide (corresponding with the 10-gramme cup of the Denver firm). The smaller size is amply sufficient for all lead ores properly so called—*i.e.*, over 10 per cent. lead contents, while the larger size is required for slags and poorer ores. There is no agreement about the best composition for lead flux, but the author adds to 5 grammes of ore, 20 grammes of flux made according to Plattner's original formula—viz., 2 parts potassium carbonate, 2 parts sodium bicarbonate, 1 part powdered borax glass, and 1 part flour. Furman,* however, recommends a lead flux with only half the above proportion of borax, while Iles† uses 30 grammes of a flux made up by the Denver Fireclay Company, in which the proportion of sodium carbonate is somewhat increased. The ore and flux should be very thoroughly mixed in the crucible with a spatula or glass rod, and well settled down by tapping. According to Iles, a cover of borax is only requisite in the case of slags and basic ores, but it is recommended by Furman to be used in all cases, except in the presence of much As, Sb, and Zn, and its use generally gives higher results, though it undoubtedly prevents the elimination of volatile metals. After well tapping down, from 1 to 4 "tenpenny" nails are added, points downward, according to Iles, for they are then less likely to retain small globules of lead than if heads downward as recommended by Mitchell and other authorities. No nails are required if the ore be oxidised; one is sufficient in the case of a slag, three if a rich sulphide ore, and four if pyritous or cupriferous. Fusion in the muffle takes from fifteen to twenty minutes if the heat be right, or may take thirty minutes if the temperature be too low. As soon as tranquil fusion is obtained the crucible is withdrawn, and the nails removed one by one with a pair of short tongs, washing each carefully in the slag to detach any adhering globules of lead. The crucible is then tapped a few times, and poured into a scorifier mould, or on to a cast-iron plate as recommended by Iles. In the latter case the button cools almost instantaneously, and is readily separated from the brittle slag, which should contain no globules. Duplicate assays ought to agree to within 0·5 per cent., and in practice they frequently agree within 1 centigramme on the button (= 0·2 per cent.).

In spite of this agreement, however, and of the fact that lead ores are always purchased on the dry assay, the process is not accurate; for there is always a large though *variable* volatilisation loss, which is compensated to a *variable* extent by the presence of other metals alloyed with the button. Iles‡ has gone into this matter in detail, determining the impurities in 700 buttons from ores averaging 34 per cent. lead, and checking

* *Op. cit.*, p. 68. † *S. M. Q.*, vol. xv., p. 341.
‡ *Loc. cit.*, p. 339.

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the dry assay by the wet assay of Alexander given below. He finds the average volatilisation loss on ores of this grade to be 7·20 per cent., which is offset by impurities in the buttons amounting to 3·75 per cent. of their weight (gold and silver 0·42 per cent., Sb, Cu, Fe, &c., 3·33 per cent.); so that the net amount by which the dry assay is too low, is in this case 3·45 per cent. of the weight of lead present. He suggests the employment of the wet assay for lead, with a uniform deduction of 2 per cent.; as is nowadays commonly done in the case of copper, to obtain the so-called "dry assay" on mattes and high grade ores.

Wet Assay for Lead.*—There are several excellent methods of determining lead in the wet way, but for works' purposes only those which are *quick* as well as accurate are acceptable. The following well-proven methods are in common use:—

1. *Gravimetric, weighing as Pb (von Schultz & Low).*†—Take 1 gramme of ore, dissolve in a 250 c.c. flask with 10 c.c. concentrated HNO_3 and a few drops of HCl, boil, add 10 c.c. strong H_2SO_4 and boil till white fumes of SO_3 are given off. Cool, dilute with 50 c.c. of water, add 2 grammes Rochelle salt, boil, filter, and wash residue of $PbSO_4$ and gangue with 1 : 10 dilute H_2SO_4. Dissolve out the $PbSO_4$ on the filter into a small beaker with a boiling solution of AmCl, decant into original flask, boil residue with a few c.c. of strong NaHO, precipitate with H_2SO_4 avoiding excess and rinse into beaker; acidify with HCl and add two or three strips of Al sheet to precipitate the lead. When precipitation is complete (five minutes is sufficient) boil a few moments, fill up flask with cold water, settle and decant into a porcelain dish to make sure of catching any particles of lead, repeat the washing several times, then invert over a tared porcelain crucible to collect the lead, rub off the Al with the fingers, settle and decant off the water. Press the Pb into one mass with an agate pestle, wash with hot water and then with 95 per cent. alcohol, dry carefully and weigh quickly. The determination takes from thirty to forty minutes, and the results are accurate, though subject to a *plus* error of from 0·1 to 0·5 per cent., due to impurities (chiefly silicon) in the aluminium, which are weighed as Pb; and to some oxidation of the lead itself.

2. *Volumetric, with Standard Ammonium Molybdate (Alexander).*‡—Ammonium molybdate gives a white precipitate with lead acetate until the whole of the lead present is thrown down, any excess of molybdate being shown at once by the yellow

* *E. and M. J.*, June 18, 1892, and *J. Am. Chem. Soc.*, vol. xv., p. 548.

† *v.* Furman, *op. cit.*, p. 137, *et seq.*; also Hofman, *Min. Ind.*, vol. iii., p. 422; and Low, *J. Am. Chem. Soc.*, vol. xv., p. 548.

‡ *Colo. S. S. M. S. Q.*, vol. ii., No. I., p. 60; also *E. and M. J.*, April 1, 1893.

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colour which it gives with a fresh solution of tannin. The indicator is made by dissolving 1 gramme of tannin in 300 c.c. of water, and is used in the form of drops on a porcelain plate. The standard solution is prepared by dissolving 9 grammes Am_2MoO_4 in 1 litre of water containing a few drops of AmHO. One c.c. of the solution should equal about 0·01 gramme of lead, but it is standardised by weighing out 0·3 gramme of pure $PbSO_4$, which is dissolved in hot ammonium acetate, acidified with acetic acid and diluted to 250 c.c. It is then *heated to boiling*, and the molybdate dropped in till a yellow colour is produced on adding a drop of the solution to one of the tannin drops on the plate. The standardisation is performed in duplicate, and the value of 1 c.c. calculated.

For the assay, take 1 gramme if under 30 per cent. Pb, or ½ gramme if over that percentage, heat in a small porcelain dish with 15 c.c. strong HNO_3 and 10 c.c. strong H_2SO_4 until the former is all expelled and white fumes of SO_3 begin to come off. Cool, dilute with a few c.c. of cold water, add hot water and boil out soluble sulphates; decant into a small filter, wash in the dish thrice with hot dilute H_2SO_4 (1 : 10), and once with a little cold water. Boil up with saturated ammonium acetate, pour through filter into a small beaker; repeat till $PbSO_4$ is all dissolved, wash with hot water, acidify with acetic acid, dilute with hot water to 250 c.c., and heat to boiling. Run in the molybdate with constant stirring, testing drops on the plate with the tannin indicator. The accuracy of the method is not interfered with by As, Sb, Zn, Cu, or P, which all pass into the original H_2SO_4 solution; Low,* however, states that it is interfered with by lime.

3. *Volumetric, with standard* $KMnO_4$ (*Knight*).†—As originally proposed, the method consisted in dissolving out $PbSO_4$ from the insoluble residue, after dissolving as above, by means of HCl, precipitating with zinc, dissolving the Pb in 10 c.c. dilute HNO_3, neutralising with Na_2CO_3 and acidifying with acetic acid. The solution was mixed with an equal volume of alcohol and precipitated with pure oxalic acid, the oxalate filtered off, washed successively with dilute alcohol and with water, dissolved in H_2SO_4 and titrated with $KMnO_4$.

Low's ‡ improvement on this method consists in precipitating the Pb with Al exactly as in his gravimetric method. He then dissolves the Pb in 5 c.c. HNO_3 (1 : 2), warms, pours into a small beaker to get out the Al, returns to flask, adds 2 drops of phenolphthalein, then a slight excess of strong NaHO, and lastly, 10 c.c. cold saturated solution of oxalic acid, cools, filters, and washes with cold water. Place in flask 75 c.c. of hot water, add

* *Loc. cit.*

† *Proc. Colo. Sci. Soc.*, Nov. 7, 1892. *E. and M. J.*, Dec. 10, 1892.

‡ *J. Am. Chem. Soc.*, vol. xv., p. 548; also *Min. Ind.*, vol. iii. p. 422.

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a few drops H_2SO_4, boil, drop in filter with contents, and titrate with $\frac{N}{10}$ permanganate.

This is an admirable method subject only to a *minus* error amounting to about ½ per cent., owing to the solubility of lead oxalate. Its great convenience is that it does away with the necessity of keeping a separate and expensive standard solution of molybdate and utilises the same solution already employed for volumetric determinations of manganese, iron, and lime, its standard in terms of Pb being that in terms of Fe × 1·848. In a works laboratory it is often a convenience to employ as few standard solutions as possible, since the amount of standardisation to be done is thus reduced to a minimum. The method, however, is not nearly so direct and rapid as that with molybdate, which is therefore to be preferred in works where large numbers of wet lead assays have to be made.

Other volumetric methods are those with $K_2Cr_2O_7$,* and with K_4FeCy_6† but although these utilise solutions already employed for other works assays (Fe and Zn respectively), they do not seem to have come into such common use as those above described.

Assay for Silver and Gold.—These metals are always determined by the dry assay, according to which they are first collected in a button of lead, which is then cupelled and the resulting bead of gold and silver weighed. The gold is afterwards "parted" from the silver by means of nitric acid, and weighed in the metallic condition; the difference between its weight and that of the bead obtained by cupellation being the weight of silver.

In the case of rich galenas, of which 400 grains or more have been taken for lead assay by the iron crucible method, the reduced button of lead contains all the values in gold and silver, and all that is necessary is to cupel this button.

For all other ores a separate assay must be made for the precious metals. Two different methods are employed—viz., the *crucible assay* and the *scorification assay*. The former is in use everywhere for gold ores, but for silver chiefly in England and on the Pacific Coast; while the latter is exclusively employed for lead-silver ores in Germany as well as in Colorado and other smelting centres of the United States. When the ore to be assayed is either poor or refractory (especially if basic); when a large part of its silver contents is in the form of chloride or combined with arsenic or antimony; or when it contains any mineral which even in fine powder decrepitates on heating, the crucible assay will generally give more uniform and more reliable results. The scorification assay is undoubtedly to be preferred

* Crossdale, *E.M.J.*, Feb. 11, 1893.

† Beebe, *E.M.J.*, July 17, 1894; Low, *J. Am. Chem. Soc.*, vol. xv., p. 548.

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for lead ores, for coppery ores, for sulphides (except such as decrepitate badly), and generally for those medium grade docile ores which contain most of their silver finely disseminated through the other minerals. On such ores the uncorrected scorification assay is higher than the uncorrected crucible assay.

Scorification Assays.—These are best performed in triplicate, in a muffle sufficiently wide to take three of the largest-sized scorifiers side by side. The muffles used in American smelting works are usually 19 inches by 12 inches wide, and they are generally heated with bituminous coal (Swansea fashion) instead of with coke. The scorifier commonly used in Colorado is the 2¼-inch size, the charge for which is $\frac{1}{10}$ assay ton (or on the 2000 lbs. ton scale, 2·9167 grammes, upon which quantity each $\frac{1}{10}$ mg. of silver obtained represents 1 oz. per ton). With ores which are very refractory, or which contain much of volatile constituents, a larger sized scorifier is necessary to leave room for the extra test lead and borax required; and some assayers habitually use the 2½-inch scorifier for poor ores and take $\frac{2}{10}$ of an A.T. for each assay so as to get larger beads to "part" for gold. When only $\frac{1}{10}$ A.T. is taken for silver it is usual to make a separate crucible assay for gold, taking $\frac{1}{2}$ A.T. each if performed in the muffle, or 1 to 2 A.T. if in the wind furnace.

The following table (substantially after Kerl) gives the proportions of granulated lead and of borax glass for $\frac{1}{10}$ A.T. of material, but a little roll of sheet lead or paper packet of borax

TABLE I.—CHARGES FOR SCORIFICATION ASSAY.

Nature of Material.	Grms. of Test Lead.	Grms. of Borax Glass.	Temperature.	Advantageous Additions, &c.
Galena, . . .	10-15	0·0-0·5		5 grms. litharge helps.
Galena, with blende and pyrites, . .	20-35	0·6-0·9		5 grms. litharge helps.
Lead carbonate, . .	10-15	0·0-0·5		
Iron pyrites, . .	30-45	0·3-0·8		
Arsenical pyrites, .	45-50	0·3-1·5	High	Cover of litharge.
Antimonial ores, .	50	1·0-3·0	High	
Blende, . . .	30-45	0·3-0·6	High	Iron oxide helps.
Lead matte, . .	25-35	0·5-1·0		
Copper ores and matte,	35-50	0·3-1·5	Low	Cover of litharge.*
Speiss, . . .	30-60	0·5-0·7	High	
Furnace accretions, .	25-50	0·3-1·5		
Tellurides, . . .	50-60	0·3		Cover of litharge.*
Siliceous ores, . .	35-40	None.		
Basic ores, . . .	35-40	0·0-2·0		Powdered glass helps.
Basic ores with barytes,	25-30	0·5-1·5		Sodium carbonate helps.
Cupel bottoms, . .	20-25	up to 0·75		

* Button has often to be scorified with more lead.

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glass can be added after scorification has commenced, when necessary. It is in fact advisable not to add at once all the borax glass, as that would result in "covering" the lead too soon; it is preferable to start with a small quantity, say ½ grain and add more afterwards as required.

The quantities of borax glass and test lead in the above table are never weighed out; the former being guessed with sufficient accuracy, while the latter is measured in an adjustable measure like that used by sportsmen for loading shells. The scorification process is conducted as follows:—

One-half of the test lead being placed in the scorifier, the ore is added and well mixed with a spatula; the other half is then added as a cover, and the borax glass on top of all. The scorifiers are placed in order in the muffle, and the door closed till the formation of a ring of slag round the surface of the melted lead shows the commencement of scorification. The door is then opened and scorification continued until the "eye" of lead is completely closed by a uniform surface of slag; upon which the muffle is again closed and the temperature raised as high as possible for a few minutes, so as to render the slag perfectly fluid. Some teachers of assaying recommend "cleaning the slag" by the addition of a few grains of charcoal or anthracite wrapped in tissue paper before the final increase of temperature, but, providing the slag is perfectly fluid, the omission of this precaution is not found to make any appreciable difference in the result. When thoroughly fluid, the scorifier is removed from the muffle and its contents are poured into the mould, which is preferably conical in shape; when cold the lead button is easily separated from the brittle slag, cleaned by hammering and brushing, and "cubed up" ready for cupellation. The slag should show no half-fused portions, and the lead should always be collected in a single malleable button, which should weigh between 8 and 12 grammes; if heavier it should be reduced by re-scorification, as the loss of silver is commonly supposed to be less in scorification than in cupellation.* If hard or brittle, it should also be re-scorified—in these cases with the addition of more lead. If the button shows traces of regulus on the top,

* Doubt has been recently thrown on the accuracy of this belief through the researches of Mason and Bowman (*Journ. Amer. Chem. Soc.*, 1894, vol. xvi., p. 313). These authors found that pure silver and gold with test lead almost invariably lost more weight when scorified down and cupelled than when the same weight of test lead was cupelled off direct. With weights of 150-600 mg. the average loss by cupellation alone was 1·99 per cent., by combined scorification and cupellation 2·54 per cent. These results are confirmed by those of Miller and Fulton (*S. M. Q.*, vol. xvii., p. 163). According to Percy (*Met. of Silver and Gold*, p. 296), the late Richard Smith found no difference in the quantity of silver obtained from test lead by direct cupellation and by cupellation after a previous scorification. The subject apparently requires further investigation.

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the assay should be rejected and another made, adding a little litharge. If the slag shows signs of imperfect fusion the assay should be repeated, crushing the ore a little finer than before, and mixing it more thoroughly with the test lead, using a little extra borax and a higher heat. The buttons of lead are then cupelled and the beads of silver weighed, the maximum difference between the three should not be more than $\frac{1}{10}$ mg. on buttons weighing 1 centigramme each (1 oz. on 100 ozs.). When the difference between the heaviest and lightest of the three does not exceed this amount their weight is added together and the mean taken; but when the difference is greater a couple more check assays should be made. All the silver beads obtained are added together for parting unless the gold is to be determined by a separate crucible assay, and in any case the amount of gold found is deducted from the combined weight of the buttons to get at the silver present. The amount of silver in the test lead should be always determined by scorifying down and cupelling 100 grammes, and the amount, if considerable, deducted from the weight of the silver beads. When, however, "pure" test lead is used the + error introduced by making no deduction for its silver contents is on all medium-grade ores very much less than the − errors through losses in scorification and cupellation, so that unless the scorifier slag and cupel bottom be re-assayed, and the amount added to that found in the original assay (which is not usually done in ordinary commercial work), a closer approximation to the truth is obtained by making no deduction for the silver contained in the granulated lead.

Crucible Assays.—The special applicability of this method to certain classes of ores has been already noted. Many different fluxing mixtures are in use, but among the best are those given in the following table. Careful examination of the sample with a lens and by washing a little of it in a small porcelain dish or saucer will usually give sufficient information as to its composition to serve for fluxing, which can easily be done to suit; bearing in mind that soda is a flux for silica, borax and powdered glass for iron and other bases; that sulphur in the ore acts as a reducer, but is counteracted by nitre as well as by oxides of iron and manganese.

There are two principal systems of fluxing; the old system advocated by Mitchell aims at keeping an excess of litharge always present to flux base metals, by which means the slags are always fluid at a low temperature, but the destruction of pots is very great, and the proper weight of lead button can in the case of many ores only be obtained after one or more preliminary trials. In the more modern system, practically the whole of the litharge added is reduced, and the base metals are kept in solution in the slag either as silicates or sulphides. The button by this method is always obtained of the correct weight,

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but it may contain copper, antimony, or other impurity, in which case it should be scorified, before cupelling, with a little lead, and should any matte or speiss be found overlying the button this should be also in such a case scorified together with the lead.

TABLE II.—Charges for Crucible Assays.

	General Formulæ.		Quartzose Ores.		Pyritous Ores.		Basic Gold Ores.	Roasted Concentrates.	Slag.
Reference,	1.	2.	3.	4.	5.	6.	7.	8.	9.
Ore,	1	1	1	1	1	1	2	1 or 2	2
Litharge (red lead),	5	1½	1	1	8	1½	1	1	½
Charcoal,	...	...	1/10	...	...	...	...	...	...
Flour,	...	1/10	...	1/12	...	...	1/10 to ¼	...	...
Lead flux,	...	...	...	..	...	1	...	1	2
Soda carb.,	1	3	¾	2	2	2	1	1	1
Borax glass,	1	½	¼	¼	1	...	1	½	1
Powdered glass,	...	...	...	...	1	...	1	1	...
Silica,	...	...	...	...	...	1	...	...	...
Nitre,	...	...	...	...	1½	...	...	...	...
Iron nails,	...	1 to 3	...	1	1 to 3	3 to 4	...	1 or 2	1
Cover,	salt	salt	borax	...	salt	salt	borax	borax	borax
Remarks,	*a*				*b*	*c*	*d*		

References.—1. Mitchell, *Manual of Assaying*, 1881, p. 546. 2, 4, and 5. Aaron, *Assaying*, Part I., San Francisco, 1889, pp. 65, 68, 62. 3. Percy, *Metallurgy of Silver and Gold*, p. 245. 6. Furman, *Manual of Practical Assaying*, N.Y., 1893, p. 129. 7, 8, and 9. Author, 1889-1893.

Remarks.—*a*. Flour or nitre to be added according to proportion of sulphur present. *b*. Without previous roasting. *c*. After previous roasting. *d*. The proportion of flour varies according to the nature of the base; with lime and alumina one-tenth part is sufficient, with all iron one-fourth part is required, and even more with ores containing manganese oxides.

Pyrites and mispickel ores may be oxidised by nitre as in mixture 5; a large pot must be used or the mixture is liable to boil over, but when a muffle is handy (as is usually the case) the author prefers to place the weighed sample in a large roasting dish just inside the muffle door and to roast out the sulphur and arsenic, melting the residue with a mixture intermediate between 4 and 8, according to the proportion of waste in the sample. Slags and poor iron fluxes require at least two assays of 1 ton each to be taken, adding the buttons together for weighing, and it is even better to make duplicates of 2 tons each, using slightly larger crucibles:

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The crucibles should be heated up before use in the same "nests" in the furnace which they will subsequently occupy during the fusion; if taken out with care they can, after charging, be replaced in the hot coke up to within an inch or two of the top without difficulty. It is important that the coke at the top of the fire be at a bright red heat, as otherwise the bottom of the charge melting while the top is still cold will effervesce, and there will be danger of "frothing over." The charge should be completely melted in from twenty to thirty minutes, after which it is well to leave it in the fire for at least ten to twenty minutes before taking it out, tapping, and pouring. The slag, if glassy and homogeneous both in texture and colour, may be thrown away; otherwise it must be powdered, mixed with a little more litharge and lead flux, and remelted. In the case of all ores and products containing over 100 ozs. silver or 5 ozs. gold, the slag must be remelted as described.

The litharge or red lead used should always be tested for silver by fusing 4 A.T. with $\frac{1}{10}$ A.T. of flour and 1 A.T. each of carb. soda and borax, the resulting lead button being scorified down and cupelled. The amount of silver found is deducted from the weight of the silver bead obtained. Litharge always contains an appreciable amount of silver; red lead, however, is sometimes so pure as to show only the minutest trace from the 4 A.T. taken, hence its use is preferable.

In Colorado, crucible assays for silver and gold are often made in the muffle, the quantity taken being then $\frac{1}{2}$ A.T., as a larger quantity could not well be fluxed without using a crucible too large for the muffle. A good list of crucible charges on the muffle system is given by Furman.*

Copper ores and furnace products are best treated by the special method which will be described for the assay of silver in copper matte.

Cupellation.—The best cupels are made of bone ash passed through a 40-mesh sieve, and moistened with water to which a little K_2CO_3 is sometimes added. They must be very slowly and carefully dried before using, and should weigh a little more than the lead buttons which they are to receive. They must be brought to a bright red heat in the closed muffle before charging the lead buttons, and immediately this operation is completed the door should be again closed, and not re-opened until the surface of the melted buttons is seen to become bright. The temperature is then regulated so that the fumes rise largely to the muffle arch, a glowing piece of charcoal being sometimes placed in the mouth of the muffle should it appear to be too cool in front. If the temperature be too low there will be risk of the button "freezing," in which case the assay is unreliable,

* *Manual of Assaying*, p. 129.

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and must be repeated; while, if too high, the volatilisation loss is much increased. The best rule is probably that universally accepted among American assayers—viz., to leave a slight but perceptible ring of feathery litharge crystals round the edge of the cupel, marking the area covered by the original lead button. Beads of silver cupelled at this heat always retain slight traces of lead, but the *plus* error thus introduced is much less than the *minus* loss by volatilisation (not to speak of the much greater loss by cupel absorption), so that a rough approximation to accuracy is obtained.

Just before the end of the operation the button exhibits a bright play of colours, caused by the formation of very thin films of litharge, and at this point the cupel should be pushed back into the hottest part of the muffle and left there for a minute or two to expel the last traces of lead. It is then withdrawn gradually towards the front of the muffle to prevent loss by "spitting" or "sprouting" at the moment of solidification, and, if at all large, is best covered with another hot cupel upside down, so as to cool it as slowly as possible.

The bead is removed from the cupel when cold by sharp-nosed pliers, and squeezed and brushed to remove adhering bone ash, if large enough; if too small, it is carefully picked up by fine forceps, placed on a blowpipe anvil and flattened by a blow from the light hammer, after which it is weighed on the assay balance to within $\frac{1}{20}$ mg. Very minute beads are weighed on the gold assay balance, which is sensitive to within $\frac{1}{100}$ mg., corresponding to $\frac{1}{10}$ of an oz. gold on $\frac{1}{10}$ A.T. taken.

Parting.—The bead should be flattened before parting, and, if it does not already contain at least two and a-half times as much silver as gold, a small fragment of pure silver foil is added and fused together with the bead on a cupel by means of the blowpipe flame.

Parting may be done either in a small $\frac{3}{8}$-inch test tube, or in a porcelain crucible. The former method is preferable when the bead is large, owing to the danger of loss by projection when boiling a quantity of acid in a crucible; but small beads are best parted in a crucible, because of the danger that particles of gold may stick to the sides of the test tube and escape observation, and because only one acid (of 1·20 sp. gr.) is required for small beads. Large beads are parted by boiling, first in acid of 1·16 specific gravity till apparently no more action takes place; the acid is then carefully decanted off and replaced by acid of 1·27 specific gravity, with which boiling is continued for five minutes longer. The acid is then poured off and the gold washed twice with hot water, being allowed to settle *very thoroughly** each time before decantation, after which the tube filled with water is in-

* Stress must be laid upon this; *v.* Ledoux, *Trans. A.I.M.E.*, vol. xxiv., p. 873.

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verted over a porcelain crucible, which is then also filled with water, and, after tapping the tube a few times, it is allowed to stand for a minute or two. When no more particles can be discerned settling through the water, the tube is removed and the water poured off, the last drops being drawn up by a capillary glass tube, and the crucible dried on a hot plate. When quite dry the gold is ignited over a spirit lamp, or in the muffle, and weighed on the "gold balance" to ·01 mg., its weight being subtracted from that of the combined gold and silver bead obtained by cupellation to get at the silver.

Assay of Matte and other Coppery Substances for Silver.—At Western (American) works the sample is scorified down with large excess of lead in 10 lots of $\frac{1}{10}$ A.T. each, collecting the buttons in pairs at the end, and assaying separately the cupels and slag of each pair. This method gives the best results for gold, but higher results for silver are usually given by the following process, which has been in use for many years at copper works where silver assays have to be made on rich copper ores and furnace products:—

Take from 1 to 2 A.T. of pulverised matte or copper borings, dissolve in strong nitric acid free from chlorine, evaporate in a porcelain dish over the sand bath to expel all excess of HNO_3, then dilute to about 1 litre, add 20 c.c. of a standard solution of lead acetate, then 1 gramme NaCl dissolved in water; stir or shake well, then add 2 c.c. of strong H_2SO_4, or, better, 5 grammes of Na_2SO_4 dissolved in water; mix well, and allow to stand twelve hours. Decant off the clear liquid, filter off the precipitated $PbSO_4$ which will have carried down with it all the AgCl and free gold in suspension, and wash it well with hot water, picking out the globules of sulphur with a forceps. Burn these in a porcelain crucible, add the residue to the precipitate, which dry and mix in a small glass or porcelain mortar with thrice its own weight of lead flux, adding also the ashes of the filter carefully burnt. Charge the mixture into a small crucible with a borax cover and an iron nail to keep out copper from the button, and fuse it in the muffle like a lead assay. If the button is over 10 grammes in weight, or if hard from the presence of copper, it is scorified down (lead being added in the latter case), and the resulting button is cupelled and parted in the usual way. The hard part of the cupel, together with the slag from the fusion of the precipitate and the scorifier slag, if any, are pulverised, mixed with 2 parts lead flux, 2 parts borax glass, and $\frac{1}{2}$ part litharge, and fused down in the same crucible. The button of lead is cupelled, and the silver obtained added to the original assay.

Whitehead* recommends separating the gold before precipitating the silver, and using KBr instead of NaCl for this

* *Chem. News*, 1892, vol. lxvi., p. 19.

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purpose. His method requires two additions of lead acetate and sulphuric acid, two separate settlings of twelve hours each, and two fusions and cupellations, one for the gold, and one for the silver. The author has found it more convenient to get both Au and Ag together in a single button after only twelve hours settling, but the use of KBr (or K I) is a decided improvement, as it obviates the danger of losing gold through Cl set free, and gives higher results for Ag owing to the lesser solubility of AgBr (Ag I) than of AgCl in solutions of copper nitrate. It is best to perform the assay in duplicate from the beginning so as to get a check on both silver and gold.

Losses of Silver in the Commercial Assay.—Whenever accurate results are desired, it is necessary to take the whole of the slags produced in the assay (whether from crucible or scorifier, or both) together with the hard portion of the cupel, and, after powdering, make a separate assay of the mixture as of a basic lead ore, adding some fluorspar to assist in melting the refractory bone ash. The lead button is cupelled at a low temperature, and the silver bead obtained is added to the original assay. Where extreme accuracy is desired, it is even necessary to repeat the correction. The assays made at metallurgical works for ascertaining the value of purchased ores (and generally for all other purposes) are almost invariably *direct uncorrected* assays; hence, the works have a considerable margin to work upon, and the working results obtained appear to be more satisfactory than they really are.

Some interesting recent researches,* however, show that the commercial assay for silver is even more inaccurate than has been supposed. For details the student should consult the original papers, but it may be briefly stated that of the three sources of error, viz.:—(1) Loss from absorption by the cupel, (2) loss in the slags, and (3) loss by volatilisation—it is clearly shown by Dewey that the first is generally by far the most important, the others following in the above order. Some of his results are given in the following table compared with similar results by Stetefeldt. †

The loss of gold in slag and cupel is much less than that of silver, as shown by the experiments of Miller and Fulton,‡ but in practice the differences in commercial gold assays are much larger in proportion, owing, no doubt, to errors of manipulation and to the smaller quantity of metal operated upon. Furman § found losses in cupelling amounting to from 1½ to 7 per cent. of the silver, and 0 to 12 per cent. of the gold; he places the aver-

* Dewey, *Journ. Amer. Chem. Soc.*, 1894, vol. xvi., pp. 505 to 516; Stetefeldt, *Trans. A. I. M. E.*, vol. xxiv., pp. 530 to 538; Furman, *ibid.*, pp. 735 to 742; Oemichen, *Zeitschr. f. angewandte Chemie*, 1893, p. 723.

† *Loc. cit.*, p. 537. ‡ *S.M.Q.*, vol. xvii., Jan., 1896, p. 169.

§ *Trans. A.I.M.E.*, vol. xxiv., p. 735; also *E. and M. J.*, Nov. 3, 1894.

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TABLE III.

Material.	Value per ton ounces.	DEWEY.		STETEFELDT.
		Losses in Slag and Cupel.		Total Losses.
		Range of Losses.	Average.	Range of Losses.
Tailings, . . .	1 to 20	18·0- 8·6	13·7	21·8-8·4
Washed ore, . . .	15 ,, 35	13·0-10·0	10·4	19·7-5·0
Raw ore, . . .	20 ,, 50	16·0- 5·0	9·7	16·8-9·0
Roasted ore, . . .	20 ,, 45	12 0- 6·0	9·1	10·6-5·4
Lead carbonates, . .	50 ,, 100	5·1- 2·6	3·8	4·8-2·9
Base sulphides, . .	1000 ,, 5500	5·0- 1·8	3 0	5·1-2·2
"Regular" sulphides, .	2000 ,, 16,000	2·8- 1·2	1·7	4·9-1·2
Copper-silver bullion, .	9000+	2·0	2·0	...
Fine bullion (999·3 fine),	29,100+	1·1	1·1	...

age loss of silver at 2·58 per cent., which agrees fairly well with the results of Dewey.

On *lead bullion* Oemichen * gives cupellation losses varying from 5 to 10 per cent. of the silver, and from 2 to 5 per cent. of the gold; Hofman † gives the loss on a pure 44 ozs. bullion as 3·5 per cent. of the silver. In the cupellation of argentiferous copper and lead, Rössler ‡ found losses as under:—

TABLE IV.

Material.	Oz. Ag. per ton.	Charge Employed.		Ratio of Ag to Pb 1:	Percentage Loss of Silver.
		Mgrms. Ag.	Grms. Pb.		
Copper, . .	43·75	10+10 Cu	200	12,000	8·3
Copper, . .	583·32	200+10 Cu	160	800	4·5
Lead, . .	43·75	150	100	600	2·5
Do., . .	87·49	150	50	300	2·2
Do., . .	218·74	150	20	120	2·0
Do., . .	437·49	150	10	60	1·6
Do., . .	874·98	150	5	30	0·9
Do., . .	4374·90	150	1	6	0·4

Ledoux § found losses of 1·75 per cent. in assaying copper

* *Zeitschr. f. angewandte Chemie*, 1893, p. 723.
† *Trans. A.I.M.E.*, vol. xxiv., p. 868.
‡ Quoted by Hofman, *Metallurgy of Lead*, p. 249.
§ *Trans. A.I.M.E.*, vol. xxiv., p. 875.

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bars with 92 ozs. silver, and of 1·12 per cent. in the case of matte with 182 ozs. silver. In direct scorification of pig copper containing from 70 to 80 ozs. per ton with test lead the author has found the uncorrected results to range from 5 to 8 per cent. lower than the assay by the combined wet and dry method above described, the chief source of loss here being, no doubt, the enormous amount of scorifier slag produced.

CHAPTER II.

THE PROPERTIES OF LEAD AND ITS PRINCIPAL COMPOUNDS.

LEAD as a material for the manufacture of sheet and pipe has been known from very early times, and was worked very largely in Spain and Greece many centuries before the Christian era.

Physical Properties.*—*Colour.*—Lead is bluish-gray in colour, and a freshly cut surface shows a bright lustre, which rapidly tarnishes on exposure to the air.

Hardness.—Lead figures at only 570 on Bottone's scale, lying between tin and thallium and far below all the other common metals; it is so soft as to be readily scratched by the finger nail, while it readily marks paper with a grey streak. Only the pure metal, however, exhibits this quality to perfection, the commercial article contaminated with Sb, As, Cu, and Zn being distinctly harder, the degree of hardness increasing with the amount of impurity present.

Malleability and Ductility.—Lead is very malleable, being readily rolled into thin foil; according to Spring,† lead filings can be formed into a solid block under a pressure of 13 tons to the square inch, while two and a-half times that pressure liquefies the metal. It is, however, low in the scale of ductility, owing to its want of tenacity, which prevents it from being drawn into fine wire.

Specific Gravity.—Lead is the heaviest of all the common metals, its specific gravity varying between 11·254 and 11·395, according as it is cast or rolled. Knab gives 11·352 and Reich 11·37 as the specific gravity of pure cast lead at 0° C., but the specific gravity of the commercial article is always lower on account of the impurities.

* *v.* Percy, *Metallurgy of Lead*, 1870, where the properties of this metal are given in great detail.

† Quoted by Roberts-Austen, *Introduction to the Study of Metallurgy*, 4th edition, 1898, p. 79.

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Fusibility and Volatility.—According to Le Chatelier, the melting point of lead is 326° C.,* and it is supposed to boil somewhere between 1450° and 1600° C., but cannot be distilled. If, however, a mixture of zinc and lead be subjected to distillation at a high temperature, the zinc vapour carries over with it a considerable quantity of lead vapour; hence the source of part of the losses in lead smelting. When cooled slowly from the melting point, lead crystallises in groups of imperfect octahedra.

Conductivity.—Taking the conductivity of silver for heat as 100, that of lead at 12° C. is only 8·5, and with the same standard its conductivity for electricity is 10·7. Taking Hg at 0° C. = 1, the conductivity of lead is 4·818.†

Other Physical Constants.—The specific heat of lead between 0° and 100° is 0·034, its latent heat of fusion is 5·369, linear coefficient ·0000292, and coefficient of cubical expansion for 1° C. ·000089.

The atomic weight of lead is 206·4, its atomic volume 18·1.

Chemical Properties.—Lead undergoes no change in dry air or in water perfectly free from air, but is rapidly tarnished by air containing moisture and by water containing dissolved air; the dull grey coating which forms on its surface being probably the suboxide, Pb_2O, which afterwards becomes converted into carbonate. Melted at a low temperature in contact with air, iridescent pellicles of suboxide form on the surface, which at a dull red heat are converted into PbO; and this PbO, when removed from the lead by continued exposure to the air at the same temperature, forms the red oxide or minium, Pb_3O_4. Other oxides of little importance are the sesquioxide, Pb_2O_3, and the peroxide, PbO_2.

Lead is readily dissolved by moderately dilute nitric acid, but is little affected by dilute HCl and by H_2SO_4 of less than 60° B.; these acids form coatings of $PbCl_2$ and $PbSO_4$ respectively, on the surface of each particle, which protect it from further action. Boiling concentrated HCl and H_2SO_4, however, attack lead slowly even in large masses, and dissolve it with fair rapidity when in a fine precipitated condition. Acetic, citric, tartaric, and other organic acids act upon it slowly in contact with moist air.

Alloys of Lead and Impurities in the Commercial Article.‡—Two kinds of lead are known in the market—viz., *soft* and *hard*, or antimonial lead. The former is in part produced direct from pure non-argentiferous ores like those of the Mississippi valley, though chiefly from the refining of argentiferous lead; the latter is always a bye-product of the refining

* *E. and M. J.*, Oct. 11, 1890.

† Roberts-Austen, *op. cit.*, p. 73.

‡ *v.* Percy, *Metallurgy of Lead*, 1870; also Hofman, *Metallurgy of Lead*, N.Y., 1892.

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operations. Soft lead is employed for making sheet lead, pipe, shot, &c., for the preparation of pewter and solder, and for the manufacture of white lead. Hard lead is only used for making type metal, Babbitt metal, and other alloys, the demand for which purposes readily absorbs the very small quantity produced.

The chief impurities in commercial lead are in the approximate order of their quantity Sb, Cu, Bi, Fe, Ag, Zn, Ni, Cd, As, Co, Mn, and S. The proportions in which they are found are given in the following table of analyses (Table V.). It is an interesting fact that all the impurities in a bar of commercial lead, except silver, are concentrated towards the top of the bar; this matter will be dealt with in greater detail in Chap. x.

TABLE V.—Analyses of Various Brands of Commercial Lead.

	Raibl, Carinthia.	Lone Elm, Missouri.	Przibram, Bohemia.	Clausthal, Harz.	Argentine, Kansas.	Port Pirie, S. A.
Reference,	1.	2.	3.	4.	5.	6.
Process,	A.	B.	C.	D.	D.	D.
Pb, . .	99·98299	99·97204	99·9841	99·98275	99·99249	99·9913
Cu, . .	·00069	·01782	·0024	·00028	·00022	·0004
Sb, . .	tr.	·00146	·0056	·00497	·00127	·0051
As, . .	tr.	·00011	...	...	tr.	tr.
Bi, . .	...	...	·0023	·00858	·00308	...
Ag, . .	·00025	·00056	·0018	·00030	·00020	·0008
Fe, . .	·00055	·00686	·0017	·00126	·00178	·0015
Mn, . .	...	...	...	...	·00021	...
Ni, . .	...	·00077	·0011	·00018	tr.	...
Co, . .	...	·00005	...	...	...	...
Zn, . .	·00076	·00033	·0010	·00086	·00075	·0009
Cd, . .	...	...	...	·00082	...	...
S, . . .	·01476	...	...	...	...	tr.
	100·00000	100·00000	100·0000	100·00000	100·00000	100·0000

Process.—A = reverberatory; B = hearth; C = blast furnace—Pattinson; D = Blast furnace followed by Parkes' process.

References.—1. *Oesterr. Jahrbuch des K.K. Berg-Akademien*, vol. xxii., p. 389. 2. *Trans. A.I.M.E.*, vol. xviii., p. 687. 3. *Oesterr. Zeitschr. f. B.- u. H.-wesen*, 1885, p. 208. 4. Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 447. 5. *E. and M. J.*, July 14, 1882. 6. *Private notes*, 1896.

Silver.—This metal alloys well with lead in all proportions,

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but, according to Levol,* none of the alloys are quite homogeneous, a fact which, while it complicates the sampling of lead pigs containing silver,† goes to show that there is no definite chemical alloy between these metals, but that each dissolves the other in a molten condition. The affinity of lead for silver is so great that it removes the latter metal from its salts and combinations with sulphur, arsenic, and even from its alloy with copper. As a rule, commercial lead contains from 1½ to 12 dwts. of silver per ton, and rarely as much as 1 oz. The small quantities present appear to protect the lead somewhat from the action of sulphuric acid, but have no other perceptible effect.

Antimony.—No definite alloys of lead and antimony are known, but the metals appear to mix in all proportions. Less than ·005 per cent. of antimony has no apparent effect, larger amounts increase the hardness of lead, diminish its malleability, and render it unfit for white lead making.‡ Lead with 0·1 per cent. Sb resists the action of cold sulphuric acid better than pure lead, but is more easily attacked by hot acid (*Lunge*). A bar of lead containing a small proportion of antimony shows in the centre a spot with uneven surface resembling moss. On heating to a bright red with access of air, antimony (and arsenic) are slagged off as antimoniate, $Pb_3(SbO_4)_2$ (and arseniate), of lead. This reaction comes into play in the softening and refining of lead for market.

Copper.—Copper forms no definite alloys with lead, for, although the two metals may be melted together in all proportions, part of the lead (containing, however, upwards of 2 per cent. copper) will, according to Percy's experiments, always separate out on slow cooling, leaving the copper (retaining lead up to as much as 25 per cent.) in the condition of a porous mass. Lead containing 1 or 2 per cent. of copper can be freed from that metal by carefully melting down at a low temperature and skimming, the residual lead, however, always retains about 0·08 per cent.§ Copper may be more perfectly separated by means of zinc, as in Parkes' process (which see). Lead for making white lead or flint glass should not contain more than ·0014 of copper,‖ but a larger proportion appears to have but little effect when it is used for other purposes; like antimony, a small quantity of copper protects lead from the action of H_2SO_4, except when hot and concentrated.

Bismuth.—Even ·0075 per cent. of bismuth affects the quality of lead for white-lead making. According to Napier,¶ 0·1 per

* Percy, *Metallurgy of Silver*, p. 173. † *v.* Chap. x.

‡ Hampe, *Zeitschr. f. B.- H.- u. S.-wesen*, vol. xviii., p. 209; also Lunge, *E. and M.J.*, Jan., 1893.

§ Hofman, *op. cit.*, p. 22; also Huntington, *E. and M. J.*, March 30th, 1895. ‖ Hampe, *loc. cit.* ¶ *Chem. News*, 1880, p. 314.

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cent. of bismuth acts like copper and antimony in protecting lead against the action of cold sulphuric acid. In larger quantity, 0·1 to 0·35 per cent., bismuth makes lead slightly harder, somewhat crystalline and more fusible, though, according to the researches of Burggraf,* its malleability is not affected by admixture of bismuth, even in proportions up to 2 per cent. When present, bismuth is not removed from lead by the Parkes process, but may be to a great extent separated by slow cooling of the molten lead, which produces crystals purer than the surrounding medium, as in the Pattinson process (which see).

Iron.—The small quantity of iron usually found in commercial lead exercises no influence upon its physical properties. Above 0·003 per cent. would, according to Landsberg,† unfit the lead for white-lead making.

Zinc.—This metal, even in small quantities, gives lead a white colour, and makes it so hard as to be unfit for rolling, rendering it, moreover, easily attacked by both cold and hot H_2SO_4. The limit of zinc for white-lead making is the same as that of iron. Lead and zinc form no definite alloys, and cannot, like lead and copper, be melted together in all proportions. Rössler and Edelmann ‡ have determined the solubility of zinc in molten lead at various temperature, and find it to vary from 0·6 to 0·8 at 400° C., up to 3 per cent. at 700° C.

Tin.—This metal is of very uncommon occurrence in commercial lead, but when present it hardens the lead, increasing its fusibility and its liability to attack by acid. Like antimony and arsenic, it is readily removed by oxidation at a bright red heat. Many supposed alloys of lead and tin have been described, but,

TABLE VI.—ALLOYS OF LEAD.

	Pb.	Sb.	Sn.	Cu.	As.	Zn.	Bi.
Type metal, . .	70·0	18·0	10·0	2·0	...	...	...
Stereotype metal, .	82·0	14·8	3·2	...	...	...	...
Bearing metal (heavy slow work), . .	84·0	16·0	...	...	...	...	...
Bearing metal (quick and light work), .	60·0	20·0	20·0	...	...	...	...
Shot metal, . .	99·6	...	...	...	0·2-·35	...	...
Solder, fine, . .	33·3	...	66·6	...	...	...	...
Do., plumber's, .	66·6	...	33·3	...	...	...	...
Pewter, . . .	20·0	...	80·0	...	...	...	...
White metal, . .	33·0	10·6	53 0	2·40	...	...	...
Babbitts' metal, . .	5·0	3·0	19·0	4·0	...	69·0	...
Fusible metal, Newton's,	31·25	...	18·75	...	...	...	50·0

* Quoted by Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 277.
† Quoted by Hofman, *op. cit.*, p. 24. ‡ *E. and M. J.*, Nov. 15, 1890.

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according to Wiesengrund,* only that with 63 per cent. Sn, corresponding to the formula $PbSn_3$, can be considered a definite chemical alloy. It solidifies at 178½° C., and melts at 183° C., the melting point being raised by addition of either of the component metals, and its specific gravity is less than that indicated by its percentage composition.

Alloys of Industrial Importance.—Table VI. (p. 25) compiled from those given by Prof. Roberts-Austen† gives the composition of the principal commercial alloys of lead.

COMPOUNDS OF LEAD.

Lead Oxide, PbO.—This, the simplest oxide, is also the only one of any metallurgical importance. It occurs in two distinct forms as *massicot* and *litharge*. The former is an amorphous yellow powder produced by exposing melted lead at a dull red heat to the action of air, continually removing the film of suboxide and oxidising it to the yellow oxide at a low temperature, avoiding fusion. On raising the temperature to a bright red heat the oxide melts, and, on cooling, solidifies as litharge, which varies in colour according to the rate of cooling, slow cooling bringing out a red, and rapid cooling a yellow colour. On a commercial scale, litharge is formed by cupelling argentiferous lead. The molten litharge produced is of an orange colour and transparent while hot; when run out from the furnace over an iron plate, or when dropped into water, it forms opaque, greasy-looking, yellow lumps. When allowed to form large cakes of a ton or more in weight, and to cool slowly, the outside portion forming a solid crust is of the usual yellow colour, while the interior swells and breaks up into loose red flakes. The swelling is caused by expulsion of oxygen which has been absorbed by the molten litharge and is given off on cooling. The specific gravity of litharge is 9·36, its melting point, according to Housell,‡ is 954° C., or slightly above the melting point of silver, and it volatilises at a white heat. In its molten condition it is a good conductor of electricity. Litharge is very slightly soluble in water (1 part in 12,000), but dissolves readily in nitric and acetic acids.

Litharge is a strong base, rapidly corroding bricks and clays, and forming the silicates described below; it also forms readily fusible compounds with all the metallic oxides. With potash and soda it apparently acts as an acid, with stannic oxide and arsenic and antimonic acids, as a base, while in other cases it seems to act simply as a solvent. The following table§ shows the proportions of litharge required to form fusible compounds with the principal metallic oxides:—

* *Berg- u. Hüttenmännische Zeitung*, 1894, p. 305. † *Op. cit.*, p. 106.
‡ *Berg- u. Hüttenmännische Zeitung*, 1866, p. 106.
§ Hofman, *op. cit.*, p. 16, quoted from Percy, *op. cit.*, pp. 17 to 18.

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1 part of	Cu_2O.	CuO.	ZnO.	Fe_3O_4.	Fe_2O_3.	MnO.	SnO_2.	Sb_2O_3.	Sb_2O_4.	As_2O_3.	As_2O_5.
Requires parts of litharge,	under 1·5	under 1·8	8	4	10	10	12	any	5	·4 to ·8	·25 to 1·0

Litharge is easily reduced to the metallic state by all reducing agents (by CO at only 100° C., by H at 310° C.),* and, therefore, forms a valuable oxidising agent. When mixed with S, Te, As, Sb, Bi, Cu, Zn, or Fe, these substances become wholly or partially oxidised, and their oxides either volatilise or dissolve in the excess of litharge, a corresponding amount of lead being reduced and combining with any unoxidised portion of the added element.

Minium, Pb_3O_4, may be regarded as a combination of 2 mols. PbO with 1 mol. PbO_2. It is a bright red powder formed by submitting the amorphous simple oxide (massicot) to oxidation at a temperature of about 300° C. At a higher temperature it loses oxygen, becoming reconverted into PbO.

Lead peroxide, PbO_2, may be prepared by digesting minium with dilute nitric acid until no more is dissolved, or by acting upon a solution of lead acetate with calcium hypochlorite. The amorphous powder left in an insoluble condition has the above composition when washed and dried; it acts as a feeble base with acetic acid, but as an acid with oxides of the alkali and alkaline earthy metals. It is a powerful oxidising agent, and, as it detonates with phosphorus, it is utilised in the manufacture of lucifer matches.

Lead Sulphide, PbS.—This substance is found native as galena (sp. gr. 7·3 to 7·7), and it may be formed artificially by melting together lead and sulphur in proper proportions, by reducing lead sulphate with any reducing agent, and by precipitating any solution of a lead salt with H_2S.

Lead sulphide, although not so fusible as the metal, readily melts at a bright red heat (935° C. according to Lodin), becoming very fluid, and penetrating all kinds of furnace linings to a surprising degree. According to the same author,† its vapour tension is considerable at temperatures much below this, which explains why it volatilises readily and in an unaltered condition when out of contact with air in lead furnaces, part of the vapour being carried away by the furnace gases, and part condensing to form the crystals and crusts of sublimed galena, which are of such common occurrence in the upper parts of lead furnaces.

* Roscoe and Schorlemmer, 1892, vol. ii., pt. I., p. 282.

† *Comptes Rendus*, 1895, vol. cxx., pp. 1164 to 1167, abstract in *Journ. Soc. Chem. Ind.*, vol. xiv., p. 807.

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Being isomorphous with Ag_2S, Cu_2S, ZnS, FeS, &c., lead sulphide readily mixes with these sulphides in all proportions; such mixtures form the "mattes" obtained in smelting complex sulphides. Both galena itself and lead matte are good conductors of electricity.* With the sulphides of antimony and arsenic lead sulphide forms sulpho-salts, both simple and complex, many of which occur in nature as well marked mineral species—*e.g.*, zinkenite, Jordanite, Jamesonite, Bournonite, &c.

Some authors have supposed the existence of subsulphides of lead, but Percy has shown that all such supposed subsulphides on careful heating eliquate metallic lead and leave a residue of crystalline sulphide; further, that lead and its sulphide can be melted together in all proportions, the properties of the mixtures being intermediate between those of their components, and approximating to one or other according to the predominating constituent.

Decomposition of Lead Sulphide.—Galena is decomposed by fusion with iron, the reaction forming the basis of what is called the "precipitation" process of lead smelting; which, in a modified form, is still in use at Clausthal, and which, to a greater or less extent, comes into play in the furnace work of all modern blast-furnace lead-smelting plants. The reaction is often given as PbS + Fe = FeS + Pb, but, although more perfect the higher the temperature employed, the decomposition is never complete.

The maximum amount of lead obtainable from pure galena (containing 86·6 per cent. Pb) varies from 72 to 79 per cent., the rest being retained in the iron sulphide. Nolte† explained the reaction by supposing the formation of a subsulphide of iron, but the observed facts are easily explained on the far more probable supposition first published by Münster‡ that a portion of the iron remains dissolved in the residual iron sulphide, which also may dissolve a portion of the lead. The reaction may then be—

$$4PbS + 4Fe = 3Pb + \underbrace{(PbS + 3FeS + Fe)}_{\text{matte}}.$$

In order to make use of this reaction in furnace work it is necessary to employ a high temperature; but the metallic iron required may be reduced in the furnace itself from oxides or from the basic silicate

$$(4FeO)SiO_2 + 2PbS + 2C = (2FeO)SiO_2 + 2FeS + 2Pb.$$

At a very high temperature the monosilicate (as also the more basic silicates) of iron reacts upon galena without the intervention of carbon, forming a sesquisilicate according to the following equation given by Percy:—§

$$3(2FeO \,.\, SiO_2) + 5PbS = 4FeO \,.\, 3SiO_2 + 2(PbSFeS) + SO_2 + 3Pb.$$

* Kiliani, *Berg- u. Hüttenm. Zeitung*, 1883, pp. 237, 366, 378.
† *Berg- u. Hüttenm. Zeitung*, 1860, p. 165.
‡ *Ibid.*, 1877, p. 195. § *Op. cit.*, p. 59.

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Both lime and baryta partially decompose galena; if the atmosphere be not reducing the reaction is probably

$$4PbS + CaO = 3CaS + CaSO_4 + 4Pb;$$

and in presence of carbonaceous matter, according to Berthier,*

$$2PbS + CaO + C = Pb + (PbS . CaS) + CO.$$

Galena is only partially decomposed by fusion with copper, the reduced lead alloying with the unaltered part of the copper, while the Cu_2S formed mixes with the unaltered galena. Zinc and tin also effect only a partial decomposition, the infusibility of the ZnS in the one case and the approximately equal affinities of lead and tin for sulphur in the other case preventing a proper separation of metallic lead.

Lead Sulphate, $PbSO_4$.—This occurs in nature as the mineral anglesite (sp. gr. 6·2), and may be formed by a careful partial roasting of galena. It is the most stable of all the sulphates of the heavy metals, remaining unaltered at a bright red heat. At a white heat, however, it softens and loses a part of its SO_3, becoming basic sulphate. Although undecomposed by simple heating, it is readily decomposed by silica according to the equation—

$$2PbSO_4 + SiO_2 = 2PbO . SiO_2 + 2SO_2 + O_2.$$

Upon this reaction is based the process of "slag roasting," hereafter to be described.

Carbon in proper proportions at a dark red heat (also carbonic oxide at a high temperature) completely reduces the sulphate to sulphide, according to the equation—

$$PbSO_4 + 2C = PbS + 2CO_2;$$

but if not in sufficient quantity, only the exact molecular proportion of sulphate corresponding to the weight of carbon present is reduced, the rest remaining unaltered. At a cherry red heat this unaltered sulphate reacts upon the reduced sulphide, as will be subsequently explained.

Lead sulphate is reduced at a high temperature by lead ($PbSO_4 + Pb = 2PbO + SO_2$) and by iron ($PbSO_4 + 4Fe = Fe_3O_4 + FeS + Pb$). It suffers a double decomposition with lime, yielding calcium sulphate. Lead sulphate is slightly soluble in water (1 part in 22,800), but considerably less so in dilute H_2SO_4 (1 part in 36,500, Fresenius). It is, however, more soluble in HNO_3 and nitrate solutions, and in hot HCl, while concentrated H_2SO_4 dissolves it to the extent of 6 per cent. It is also soluble in solutions of the alkaline chlorides, $CaCl_2$ and calcium acetate; in all ammoniacal salts, especially the acetate; and slightly in sodium hyposulphite, the solubility varying with the temperature and concentration of each solvent.

* *Traité des essais par la voie sèche*, Liège, 1837, vol. ii., p. 580.

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Roasting of Lead Sulphide—Reactions between Sulphide, Sulphate, and Oxide.—When lead sulphide is roasted at a low temperature, it is at first simply oxidised with evolution of SO_2 according to the equation—

$$2PbS + 3O_2 = 2PbO + 2SO_2.$$

A part of the SO_2 takes more oxygen from the air becoming SO_3, which combines with the PbO to form $PbSO_4$. According to Plattner,* pure galena yields on roasting a much smaller proportion of sulphate to oxide than is given by galenas containing much pyrites; this is probably on account of the greater tendency of SO_2 to form SO_3 in presence of iron oxides. It is possible that some $PbSO_4$ may be formed from PbS by direct absorption of oxygen, as suggested by Rammelsberg,† but this is doubtful.

When mixtures of lead sulphide with oxide or sulphate are subjected to a bright red heat (at which the mixtures soften), the following reactions take place:—

$$PbS + 2PbO = 3Pb + SO_2.$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

In the case of oxide the decomposition invariably takes place in molecular proportions, so that any excess of sulphide on the one hand or of oxide on the other remains unaltered on the surface of the lead, except in so far as it may have been affected by the material of the crucible, or other vessel in which the experiment has been made. When PbS is fused with excess of $PbSO_4$, however, another reaction takes place, viz.:—

$$PbS + 3PbSO_4 = 4PbO + 4SO_2,$$

and this reaction may take place simultaneously with the two preceding in different parts of the same charge. It is probable, indeed, that towards the end of the operation this reaction becomes developed very largely at the expense of the preceding. One very important process of lead extraction depends exclusively upon the above reactions, and, as will be seen hereafter, it is essential that the temperature be kept low during the roasting, and then raised suddenly in order to bring about the reactions.

According to Hannay,‡ all the above reactions given by Percy and other authorities are incorrect. This author has found that PbS is much more volatile at a white heat in SO_2 than in other gases, and supposes the existence of a body to which he assigns the formula $PbS . SO_2$, from which the PbS crystallises out on cooling. He supposes the principal reaction which takes place on heating together PbS and $PbSO_4$ to be the following:—

$$12PbS + 12PbSO_4 = 12Pb + 8PbO + 4PbS . 8O_2 + 16SO_2,$$

* *Die Metallurgischen Röstprozesse*, Freiberg, 1856, p. 145.
† Rammelsberg, *Die Metallurgie des Bleies*, 1872, p. 39.
‡ *Trans. Inst. Min. Met.*, vol. ii., p. 188.

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and proposes to treat galena ores by melting and blowing in a kind of Bessemer converter to obtain (1) a small quantity of lead rich in silver; (2) molten litharge; (3) fume which by excess of air is converted into lead sulphate. Huntington * regards the volatilisation of PbS in N, CO_2, SO_2, and other gases as probably a case of mere solution in a gas; and with regard to the proposed "new metallurgy of lead," points out the impracticability of the process, especially as regards the condensation of the enormous amount of lead fume formed, and the difficulty of finding any furnace lining to withstand the action of molten litharge at the temperature of molten PbS. Lodin † also confirms the reactions heretofore universally recognised as being correct at the temperatures prevailing in ordinary lead furnaces. There is no doubt that Hannay's work is interesting, as showing that the volatility of PbS is greater than it is generally supposed to be, and that it is increased in the presence of certain gases; but his explanation of the reactions taking place in lead furnaces must be regarded as untenable, and his proposed "new metallurgy of lead" impracticable. Jenkins and Smith,‡ while entirely confirming the old reactions, prove that lead is attacked by sulphur dioxide.

Lead Carbonate, $PbCO_3$.—Lead carbonate occurs as the mineral cerussite (sp. gr. 6·46). At 200° it is decomposed into PbO and CO_2, and at the same temperature is reduced to metallic lead by CO, charcoal only acting upon it at a somewhat higher temperature. The white lead of commerce is a basic salt, the composition of which is $2PbCO_3 . PbH_2O_2$.

Lead Silicates.—Lead oxide and silica begin to combine at the softening temperature of the oxide—*i.e.*, below 800° C.; and if both substances are finely divided, and the heat maintained at this temperature, combination will be effected without the mixture becoming fluid. According to Percy, all the silicates of lead up to the trisilicate, $2PbO . 3SiO_2$, are readily fusible at low temperatures, the monosilicate in particular, $2PbO . SiO_2$, being as fluid as water. Higher silicates are successively less fusible up to $2PbO . 9SiO_2$, which only melts to a substance resembling porcelain, while $PbO . 18SiO_2$ can barely be fritted at the highest temperature obtainable. All the fused silicates of lead are yellow, the presence of other metallic oxides altering the colour, as seen in the scorification process of silver assaying.

Silicates of lead are not readily decomposed by carbon or sulphur, but are decomposed by carbon in combination with lime, or some other base which combines with the liberated silica. Iron in excess effects a complete decomposition of all lead silicates at a bright red heat, forming monosilicate, $2FeO . SiO_2$.

* *Ibid.*, p. 217.

† *Comptes Rendus*, 1895, vol. cxx., pp. 1164-1167; and abstract in *Journ. Soc. Chem. Ind.*, vol. xiv., 9, p. 807.

‡ *Journ. Chem. Soc.*, 1896.

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Sulphides of iron, baryta, and lime all decompose basic or sub-silicates of lead at comparatively low temperatures, forming silicate of the base, sulphurous acid and metallic lead. The reaction in the case of iron sulphide is as follows :—

$$4PbO . SiO_2 + 2FeS = 2FeO . SiO_2 + PbS + 3Pb + SO_2.$$

The monosilicate is only partially decomposed, and requires for complete decomposition a higher temperature and the addition of a free base, such as lime :—

$$3(2PbO . SiO_2) + 4CaO + 2CaS = 3(2CaO . SiO_2) + 3Pb_2 + 2SO_2.$$

The bisilicate and lower silicates are readily decomposed by nitric acid, but decomposition is not complete in the case of the trisilicate, and higher silicates are attacked with increasing difficulty.

Lead Borates.—Lead oxide and boric trioxide melt together in all proportions, and the compounds formed are more fusible than the corresponding silicates. Advantage is taken of this fact in lead and silver assaying.

The *haloid* compounds of lead are very volatile, and form volatile chloro-sulphides and chloro-phosphates. They are readily reduced by contact with carbon and metallic bases at a red heat.

CHAPTER III.

LEAD ORES.

THE principal minerals containing lead are the following :—

Galena, PbS ; 86·6 per cent. Pb.—This, the commonest of lead minerals, is frequently found in groups of cubical or octahedral crystals; also massive, filling cavities. It is found in every country in the world, and in almost every variety of deposit, from true fissure-veins to impregnations in certain beds of limestone, dolomite and sandstone. In most cases it is so mixed with other vein, or rock matter, as to require some process of "dressing" to fit it for treatment by the smelter; and very often the admixture with other metallic sulphides is so intimate as to give rise to great loss in these preliminary mechanical operations. The subject of ore-dressing scarcely appertains to metallurgy, and the student may consult with advantage the very complete compendium given by Dr. C. le Neve Foster in his *Ore and Stone Mining.**

* Reference should also be made to Kunhardt, *Practice of Ore Dressing in Europe*, New York, 1892; to Bellom, "On the Mechanical Preparation of Ores in Germany," in *Ann. des Mines*, 1891, vol. xx., p. 1; and to two papers in the *Proc. Civ. Eng.*, viz., Curtis on "Gold Quartz Reduction," and Commans on the "Concentration and Sizing of Crushed Minerals" (*Proc. Civ. Eng.*, vol. cviii., p. 97, and vol. cxvi., p. 3, respectively).

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Galena is almost always argentiferous, and its silver contents may be present either as isomorphous sulphide, Ag_2S, or as some distinctly silver-bearing mineral (*e.g.*, argentite, stephanite, polybasite, fahlerz) finely disseminated through the cleavage planes, and this difference is important as regards the dressing operations. In the former case the loss of silver in dressing is proportionate to the loss of lead; in the latter, and by far the commoner, case, the loss of silver in dressing greatly exceeds the loss of lead, as the silver-bearing mineral, besides being finer to begin with, is also both lighter and much more brittle, so that it is driven into the finest slime, which floats away in and upon the surface of the dressing water. A notable case of this kind is to be found in the Zeehan and Dundas field of Tasmania, where, according to a series of assays of ores from different mines and workings given by Thomæ,* the handpicked ore contains on an average 94 ozs. silver per ton for 66 per cent. of lead, while the dressed ore carries only 76 ozs. silver for 70 per cent. lead, a clear loss of 25 per cent. of the silver in the fine slimes carried off by the dressing water. The poorest galena as regards silver contents is that from Bleiberg (Carinthia), which contains only 1 dwt. per ton of ore; the richest known is that from Schemnitz (Hungary), a specimen of which, according to Beudant, gave 7 per cent. of silver, or over 2200 ozs. per ton.†

It is a common belief among miners that the grain of galena is influenced by its richness in silver, the general idea being that a coarse-grained galena is likely to be poor in silver, and a fine-grained variety rich. No general rule of the kind can be formulated;‡ nevertheless, as regards certain districts, some connection is observable between the grain of the galena and its silver contents. For instance, at Broken Hill, N.S.W., the coarse-grained galenas are said to be generally richer in silver than the fine grained; while, according to the author's experience in various parts of Mexico, the contrary rule prevails as regards the ores of each particular mine, though the coarse-grained galenas from one mineral deposit may be richer than the finest-grained varieties from another.

Cerussite, $PbCO_3$; 77·5 per cent. Pb.—This mineral is seldom found pure in quantity, except when occurring, as at Leadville and Broken Hill, in secondary crystals distributed through the "gozzan" of large complex ore bodies. In these cases, though itself comparatively free from silver, it is found associated with native silver and its haloid compounds, especially the chloride and chloro-bromide. It is nearly always mixed with more or less anglesite, and with oxide of iron and other

* *Trans. Inst. Min. Met.*, vol. iv., p. 60.
† Phillips, *Elements of Metallurgy*, 1891, p. 617.
‡ *v.* Percy, *Metallurgy of Lead*, p. 97.

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vein material. Important deposits at Laurium (Greece), Eureka (Nev.), and Leadville (Colo.), are now practically worked out, but other important localities which still yield large quantities of this ore are Carthagena and Linares (Spain), Sierra Mojada, St. Eulalia, and Velardeña (Mexico), and Broken Hill (N.S.W.).

Anglesite, $PbSO_4$; 68·3 per cent. Pb.—Like the preceding, this mineral is invariably a secondary or decomposition product of galena, and it is found mixed with the carbonate everywhere, generally, however, in small proportion. When crystallised, it is, like the carbonate, nearly free from silver.

Pyromorphite, $3Pb_3(PO_4)_2 + PbCl_2$ with 69·5 per cent. Pb, and **Mimetesite,** $3Pb_3(AsO_4)_2 + PbCl_2$ with 76·2 per cent. Pb.—These two minerals are mentioned together, for, although the formulæ of pure specimens are as above, the former frequently contains As_2O_5, and the latter large quantities of P_2O_5; while both may contain lime replacing the lead and fluorine replacing the chlorine. Both are comparatively free from silver, and occur associated with cerussite in the upper decomposed portions of lead lodes, mimetesite being, perhaps, on the whole, the commoner of the two.

Other lead minerals* are *Crocoisite,* $PbCrO_4$; *Wulfenite,* $PbMoO_4$; *Stolzite,* $PbWO_4$; *Mendipite,* $PbCl_2 2PbO$; *Vanadinite,* $3Pb_3(VO_4)_2 + PbCl_2$; *Lanarkite, Phosgenite, Clausthalite,* &c., as well as sulphantimonides, such as *Jamesonite, Bournonite,* &c. Seeing, however, that none of these minerals occur in large quantities, or otherwise than associated with other ores of lead, they cannot be said to be of any metallurgical importance.

Commercial Lead Ores.—For metallurgical purposes the ores of lead are divided into "sulphide ores," consisting in the main of galena, with greater or less admixture of blende, pyrites, chalcopyrite, mispickel, fahlerz, &c., and "oxidised ores," called in America "carbonates," under which general term is included not only cerussite itself, but all its admixtures with anglesite, pyromorphite, &c.

Oxidised Ores.—It will be understood that the oxidised ores are not essentially a product of different districts from those producing sulphides, but that they are merely the surface gozzans, into which large masses of the latter have been decomposed by atmospheric agencies; anglesite representing an intermediate stage in the transformation of galena into cerussite. The change from oxidised ores to sulphides may take place gradually, as at Catorce and some other Mexican mining districts, or suddenly, as on Iron Hill, Leadville.† The depth at which the change

* For details, works on mineralogy should be consulted, especially Dana, *System of Mineralogy,* New York.

† Blow, *Trans. A.I.M.E.*, vol. xviii., p. 170.

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takes place also varies considerably; thus at Broken Hill (N.S.W.) large masses of unoxidised sulphides are found at only 200 feet from the surface, while at Eureka (Nev.) oxidised ores continued down to 1300 feet.* The principal factors which determine the depth to which oxidation extends are—(1) Depth below surface of permanent water level of country; (2) permeability of the rocks; and (3) amount of rainfall.† By atmospheric oxidation the pyrites of the original mixed sulphide ore becomes iron oxide in the gozzan, chalcopyrite forms oxide of iron and carbonate of copper, blende is partly leached away as zinc sulphate, but a part remains as calamine and smithsonite. The silver contents of the original sulphides partly remain as sulphide or sulphantimonite, partly become native silver, but more generally form haloid compounds with the small quantities of haloid elements contained in the air and meteoric water. In this way the silver of the Leadville "carbonates" was chiefly found as chloride, while at Broken Hill and in Chili the bromide and iodide are more common. Carbonate ores are generally richer in silver than the deep-seated sulphides, to the oxidation of which they owe their origin. This may be due to several causes, but the principal one is undoubtedly the much greater solubility of lead sulphate and carbonate, than of silver chloride and sulphide. Small nodules of galena are frequently found in carbonate ores, which are very much richer in silver than the surrounding matrix, but these are of secondary origin in most cases. Any gold contained in the original sulphides remains in the carbonates in the native condition.

Carbonate and other oxidised ores can be but seldom concentrated to advantage, owing to the comparatively low specific gravity of the oxidised lead minerals compared with galena, and to their great friability compared with the quartz, limonite, and other gangue.‡ The loss of silver in the fine slimes is usually more serious than the loss of lead. Attempts have been made to leach out part of the silver contents with a hyposulphate solution before concentrating for lead, also to separate most of the lead by a dry concentration process prior to working up the tailings by amalgamation or lixiviation processes; but neither attempt can be said to have been very successful.

Sulphide Ores.—With reference to these ores, it may be said that, as a general rule, those deposits in which the galena occurs most free from other metallic sulphides will be poorer in silver than those in which it is intimately associated with

* Curtis, "Silver Lead Deposits of Eureka," *Monograph VII. U.S. Geol. Survey.*

† For further information on this interesting subject the student is referred to a paper by Halse on "Deep Mining in Mexico," *Trans. Inst. Min. Met.*, vol. iii., Part III., p. 418.

‡ Concentration was, however, successfully practised at Tombstone (Ariz.), *v.* Church, *Trans. A.I.M.E.*, vol. xv., p. 601.

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pyrites, blende, and other sulphides. Deposits in sedimentary rocks are almost always poorer in silver than fissure vein deposits associated with metamorphic or eruptive rocks.

Galena occurs comparatively free from both blende and pyrites at Engis (Belgium), Mechernich (Rhen.-Pruss.), and in the upper parts of the limestone deposits (Lower Silurian) of Wisconsin and Illinois. Galena associated with blende alone is found at Raibl and Bleiberg (Carinthia) and at Joplin (Mo.), while in the mines of St. Joe and La Motte (Mo.) it is associated with pyrites to the exclusion of blende. In all these cases the galena is almost free from silver, the ratios of that metal to lead varying from 1 dwt. Ag for 70 per cent. Pb (Bleiberg, Carinthia), to 1¼ ozs. Ag for 80 per cent. Pb (Granby, Mo.), and 4 ozs. Ag for 60 per cent. Pb at Mechernich, according to a useful little table given by Hofman.* All the above are distinctly sedimentary deposits, either in sandstone, as at Mechernich, or in limestone, as at the remaining localities cited. The Spanish galena deposits in limestone (Linares, Sierra Almagrera, Almeria, &c.), which are also comparatively free from other metallic sulphides, are of an intermediate character, averaging, as prepared for smelting, from 6 to 10 ozs. Ag for 75 per cent. Pb.

When galena is found most intermingled with other sulphides (especially with complex sulphides and sulphantimonides like fahlerz), and more particularly when in contact or in connection with crystalline, metamorphic, or eruptive rocks, as in Bohemia, Saxony, Hungary, the Harz and the Rocky Mountains, it is usually richest in silver. As already pointed out, however, a large part of the silver contents of these complex sulphide mixtures does not exist as a constituent of the galena itself, but rather in distinctly silver minerals, such as argentite, stephanite, and fahlerz, either finely disseminated through the cleavage planes of the galena, or through the matrix. Even the blende and pyrites in these mixed ores usually carry appreciable quantities of silver; in some parts of the great Broken Hill Proprietary Mine the blende carries nearly as much silver as the galena. In one interesting case described by Freeland,† some ore from the Minnie Mine at Leadville was separated as nearly as possible into its component parts of galena, blende, and pyrites, and the blende turned out to be much richer than the galena. The following analyses are by Boggs.

This is, of course, rather an exceptional case, and by no means the rule in the Leadville district; thus, Taylor and Brunton report‡ a similar series of analyses from the Col. Sellars Mine, in which the galena contains 20 ozs., the pyrites 5 ozs., and the blende only 3 ozs. The series of analyses mentioned

* *Metallurgy of Lead*, N.Y., 1893, p. 26.

† "Iron Hill sulphide deposits," *Trans. A. I. M. E.*, vol. xiv., p. 181.

‡ *Eng. and M. J.*, 8th May, 1886.

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has been quoted in full merely as a warning against the too common assumption that in dealing with low grade complex ores the only thing to aim at is a successful concentration of the lead. It may frequently happen that in spite of a fairly good saving of this metal, what with the losses of silver in blende and pyrites tailings, and what with the loss of finely divided true silver minerals in the slimes, the lead concentrates do not contain more than one-half of the silver value of the original ore. It is, therefore, in many cases preferable to smelt the whole mass of a complex ore body rather than to make any attempt at concentration. Analyses of smelting ores will be given in the sections dealing with the various processes of treatment.

	Galena.	Blende.	Pyrites.	Mixed.
Pb,	72·65	6·71	2·21	50·86
Zn,	5·66	55·08	14·24	12·86
Fe,	1·60	4·00	35·40	9·30
S,	15·56	32·44	44·76	24·50
Ag,	0·14	0·324	0·014	0·039
Residue,	4·12	0 92	2·70	1·88
	99·83	99 474	99·324	99·439
Silver, oz. per ton,	41½	94½	4½	11½

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SECTION II.—LEAD SMELTING.

INTRODUCTORY.

PRACTICALLY speaking, only smelting methods are applicable to the extraction of lead from its ores. Wet methods, based on the leaching out of $PbCl_2$ or of $PbSO_4$ by means of suitable solvents and precipitation with iron, have been at various times suggested, but none have proved sufficiently promising to be worked on a commercial scale.

As already seen, by far the commonest lead ore is galena; comparatively small proportions only of carbonate, sulphate, and other ores are now accessible,* and, as a rule, only as incidental accompaniments of large bodies of galena. The treatment of these oxidised ores, moreover, offers no special difficulty and requires no special appliances; they may be treated generally as roasted sulphide ores, oxidation having been effected slowly by atmospheric agencies instead of quickly in a furnace. The smelting of these oxidised ores in Australia, Mexico, and elsewhere will be described in its proper place, and the treatment of lead ores may be considered generally as referring only to galenas.

Classification of Methods.—Three principal methods of treatment may be distinguished:—

1. The *Roast and Reaction Method*, in which the galena is first roasted so as to convert part of it into PbO and $PbSO_4$; the temperature is then raised so that these compounds react upon the unaltered sulphide with production of metallic lead and SO_2.†

2. The *Roast and Reduction Method*, in which the galena is roasted pretty completely to lead oxide, which is then reduced to metal with coke or charcoal. A small proportion of sulphate formed in the roasting is either transformed into silicate at the end of the roasting process, and then reduced in the smelting furnace with the help of iron oxide, or it may be reduced to sulphide in the smelting furnace, and so form a "matte" from which part of the metallic lead is again set free by iron. In any case nearly the whole of the lead is recovered direct in a metallic condition.

* Except, perhaps, in Mexico.

† For equations representing these reactions *v.* Chap. ii.

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3. The *Precipitation Method* in which galena is decomposed at a high temperature by the agency of metallic iron, forming metallic lead and a mixture of iron and lead sulphides, the so-called "lead matte."

These methods are rarely employed quite independently of each other, for the residues of the first method are almost always worked up by the second or third methods, and the second method is almost always combined with the third, and often with the first also.

The choice of method depends partly upon the quantity and nature of the impurities in the ore, partly upon local conditions, such as the kind of fuel available, and the price of labour.

The *Roast and Reaction Method* may be carried on in hearths or in reverberatories, and requires raw fuel only, but is suited only to high grade galenas containing 60 to 70 per cent. lead and upwards, since large quantities of other substances interfere with the reactions of PbO and $PbSO_4$ on PbS. It is quite inapplicable to ores containing much quartz or silicates, which would form a fusible lead silicate, and so put a stop to the reaction. The advantages of this method for dealing with rich ores are:—(1) Yield of a very pure lead; (2) use of cheap forms of fuel; (3) no fluxes required; (4) comparatively small volatilisation loss. Its disadvantages are:—(1) Production of a very rich slag which must be re-treated; (2) heavy labour cost; (3) large quantity of fuel required.

The *Precipitation Method*, formerly carried out in reverberatories, but now only in blast furnaces, and that to a very limited extent, requires coked fuel and much ferruginous flux. It is only applicable to rich lead ores containing comparatively small quantities of antimony, arsenic, &c., because these metals are also reduced by iron, rendering the lead very impure. Silica and other non-metallic minerals do not interfere with the process, and copper ores are well suited to it because the whole of that metal, even if existing in very small proportions, becomes concentrated together with part of the silver in the matte, from which both can be recovered. The advantages of this process are that it dispenses with a preliminary ore roasting, and gives ultimately a good extraction of lead with comparatively low volatilisation losses of both lead and silver. It has, however, many grave disadvantages, especially the high consumption of coked fuel, and the slow, because only partial and gradual, recovery of the lead, together with a complicated matte treatment which makes the method a very costly one for labour. As a separate and distinct process, therefore, the method is practically obsolete, surviving only in the Upper Harz at Clausthal under exceptional local conditions; it is, however, frequently combined to some extent with the following:—

The *Roast and Reduction Method* is applicable to all kinds

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of ore, but especially to the poor siliceous, pyritous, and blendiferous ores which are so common, and which cannot be treated by the foregoing methods. It comprises two independent processes carried on in separate furnaces. The roasting is conducted in the various ways to be described, and the smelting of the roasted ore takes place in blast furnaces, the construction of which shows great variation in detail, though the principle is always the same.

The roast and reaction method may be carried out either in reverberatories or in hearths, the residues in either case being run down in blast furnaces. Whatever the appliance employed there is always considerable loss of lead by volatilisation, which becomes of greater importance in proportion as the ores are richer in silver. In all cases, therefore, the furnace flues are connected with a more or less complete system of flues and condensing chambers for recovering the flue dust. A separate chapter is devoted to this matter, which need not, therefore, be further dealt with here.

CHAPTER IV.

LEAD SMELTING IN REVERBERATORIES.

Preliminary.—The ore for this process must be crushed sufficiently fine to pass a 4 or 5-mesh sieve, an operation which is usually performed as part of the "dressing" or "concentration" almost always required to produce ore of sufficiently high grade for the process before the ore reaches the smelting works. In all cases the process comprises two stages, which follow each other in the same furnace, and which are rapidly alternated several times.

1st Stage or Roasting.—The ore is spread in a layer of from 3 to 4 inches over the hearth of the furnace, and gradually brought to a low red heat, say 500° to 600° C., at which it is kept with free access of air, being continually raked to expose new surfaces and to prevent clotting, which would suspend the process of oxidation. The roasting is not allowed to complete itself, sufficient undecomposed sulphide being left to bring about the reactions described in Chap. ii. The rabbling in of small quantities of lead carbonate and sulphate ores or of litharge is of great advantage, as it shortens the period of roasting. Could a sufficient amount of these oxidised substances be obtained to mix with the galena in proper proportion, roasting might, in fact, be dispensed with altogether, and the reaction period entered upon at once in a hot furnace, but this is rarely, if ever, possible.

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2nd Stage or Reaction.—The temperature is raised so that the oxidised compounds may react upon unaltered sulphide according to the equations given on p. 30. The reactions take place best at the temperature when the charge begins to soften, and are incomplete if it be allowed to melt. The charge is worked up with the rabble, lime being generally added to stiffen it, and the cooling consequent on opening the doors stops the first reaction period, and brings about a second roasting, followed, when the doors are closed and the temperature again rises, by a second reaction. These operations are repeated until there is not enough lead sulphide present to react upon the ~~sulphide~~ and sulphate oxide. The last operation, then, consists of adding fine charcoal or coal, which is well rabbled into the charge with the object of reducing part of the residual lead oxide to metal.

The chief difficulty is to oxidise the charge uniformly, only just enough to secure the theoretical molecular proportions for the reaction; and as roasting goes on more or less during the whole period of reaction, it usually happens that considerable excess of oxide and sulphate is produced. This excess, together with more or less undecomposed sulphide, globules of metallic lead, and the whole of the other substances mixed with the galena, remains on the hearth in a half-melted condition as the so-called "grey slag," which is raked out for separate treatment. Sometimes this consists merely of crushing and washing to save the metallic lead, but more generally an attempt is made to get out the combined lead also. In some cases, especially with rich ores, the residues from which are small in amount, the slags are treated in the same furnace, coal dust being rabbled in and the temperature raised to secure the reduction of the combined lead; but in this case the loss by volatilisation is considerable, and a notable amount of lead still remains as sulphide and silicate in the final residues. It is far better, therefore, to leave a larger proportion of lead in the grey slag, and work this up afterwards in blast furnaces.

Influence of Foreign Substances.—*Quartz, clay*, and all other *silicates* are very injurious, as they form lead silicates which cannot be decomposed at the low temperatures prevailing in the furnace, besides glazing over particles of undecomposed sulphide, and so protecting them from the reactions. The practical limit of silica in ores which can be advantageously treated by the roast and reaction process is about 4 per cent., but a very much smaller amount is sufficient to glaze particles of ore and so obstruct the reactions, unless the heat is kept very low.

Calcite (*limestone or dolomite*) like other inert substances, retards the reactions by interfering with the direct contact between the oxidised lead compounds and unaltered sulphide. With this exception, however, it acts, on the whole, advantage-

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ously by hindering the fusion of the charge, at all events up to amounts of 10 or 12 per cent. When not present in the ore, lime is frequently added in small quantities during the process with the object of stiffening the charge and preventing fusion.

Barytes and *fluorspar* remain inert during the process, but when present together tend to increase the fusibility of the charge.

Chalybite often occurs as a gangue of galena ores, but can be mostly removed by dressing. Small quantities which remain with the ore lose their CO_2 during the roasting and become converted into magnetic oxide of iron, which assists the reaction by helping to stiffen the softened charge and, perhaps, also, by acting as an oxygen carrier.

Pyrites in small quantity has a decidedly favourable influence on both the roasting and reaction periods. During the former it becomes oxidised to iron sulphates, which subsequently give off SO_3, and so directly assist the formation of lead sulphate. During the latter, the ferric oxide formed tends to stiffen the charge and probably also to act as an oxygen carrier. In quantities above 10 or 12 per cent., however, ferrous sulphide tends to form and run down prematurely as a matte or "regulus," retaining, moreover, lead sulphide in the residues; and with 35 per cent. pyrites the roast and reaction process becomes not only uneconomical but impossible.*

Chalcopyrite behaves like pyrites, except that some copper is reduced with the lead.

Blende is partly converted into oxide and sulphate during the roasting and partly remains unaltered. Up to 4 or 5 per cent., the presence of blende assists the roasting process; but 10 or 12 per cent. retards the reactions very much; and 35 per cent., as in the case of pyrites, stops them altogether.

Antimony (stibnite, Jamesonite, Bournonite, zinkenite) is the most deleterious of all foreign elements, even in quantities of only 2 to 3 per cent. In the first place, both its oxide and sulphide are volatile, causing losses both of lead and silver. In the second place, they react upon each other, like the corresponding lead compounds, forming metallic antimony, part of which alloys with the lead, making it hard; and part volatilises again, carrying lead with it. Moreover, both oxide and sulphide are readily fusible, causing the ore to cake even during the roasting process, while the former combines with lead oxide to form lead antimoniate, which remains in the residues and causes them to yield a very hard lead when re-smelted.

Arsenic (mispickel, &c.) like antimony, is very detrimental, causing losses by volatilisation and by combination with lead oxide to form arseniate. A portion also combines with the lead and contaminates it.

Silver and *gold* in the ores follow the lead reduced to metal,

* Bouhy, *Ann. des Mines*, 1870, vol. xvii., p. 178.

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very little being left in the oxidised residue; the lead reduced first is by far the richest in precious metals, so much so that it frequently contains four or five times as much as the last lead, and seven to ten times as much as that in the residues.

Classification of Processes.—Until recently three main varieties of process have been distinguished, namely, the *Carinthian*, *English*, and *Silesian*. The first, however, is only a survival, and the last is but a trifling modification of the second. Besides these there was formerly in existence a distinct Cornish process (of which the so-called Breton process was a modification) now no longer in use.

The *Carinthian* process was only suited to pure rich ores, but from such extracted a large quantity of pure lead with a low loss, its disadvantages being the very high cost for fuel and labour. It was characterised by small furnaces and charges, and by a low temperature throughout, with the object of producing as nearly as possible 1 mol. of $PbSO_4$, or 2 mols. of PbO for each mol. of unaltered PbS, so as to get the theoretical reactions :—

$$\begin{cases} PbS + PbSO_4 = 2Pb + 2SO_2 \\ PbS + 2PbO = 3Pb + SO_2 \end{cases}$$

Coal was added to the residues in the same furnace so as to get out as much lead as possible.

This method was in use at Bleiberg, Carinthia, and also in Belgium, but has now given way * to a modified Silesian process, followed by smelting the residues in Pilz furnaces. There is, however, an American form of the process, which still exists to some small extent at isolated points in the Mississippi valley.

The *English* (*Flintshire*) process is conducted in large furnaces and at a high temperature so as to get out as much lead as possible in the shortest time and with a small consumption of fuel; the volatilisation loss is, however, rather high. Owing to the high temperature, reaction is at first chiefly between PbO and PbS, but little $PbSO_4$ being formed, except towards the end of the process.

The residues are treated in small blast furnaces (cupolas). The *Silesian process* is simply an improvement on the ordinary Flintshire method, with the object of saving labour and securing lower volatilisation losses. It is carried on in large furnaces, and at as low a temperature as possible, in consequence of which the proportion of lead obtained at first is smaller and the residues for subsequent cupola treatment are much richer.

The extinct *Cornish* process was adapted to the treatment of 60 to 70 per cent. lead ores containing some copper and other impurities. The roasting and reaction stages were carried on in separate furnaces, and a larger quantity of PbO and $PbSO_4$ was formed in the first stage than was required for reaction

* *Oesterr. Zeitschr. f. Berg-. und Hüttenwesen*, June 3rd, 1893, p. 283.

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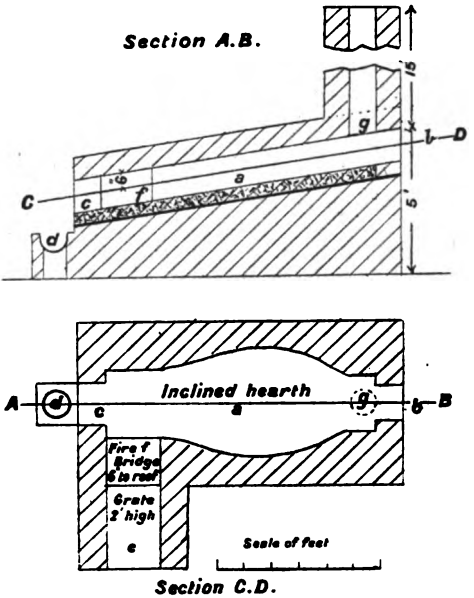
upon PbS in the second stage. This excess of PbO was reduced, partly by addition of "culm"* and partly by scrap iron, the latter of which also served to collect copper and any remaining sulphur into a "regulus," which cleaned the slag so effectually that it could be thrown away. The loss by volatilisation was, however, high, owing to the high temperature employed, and the process was more expensive than the ordinary English process.

The Carinthian Process.—This process was, until recently, used at Bleiberg in Carinthia for treating galena concentrates of from 60 to 75 per cent. lead. A good description, with illustrations of the furnace adopted, is given by Percy.† The charges in this furnace were only 3 to 4 cwts., and the slag from two successive charges was reduced in the same furnace with addition of charcoal.

An almost exactly similar process was largely in use in Missouri and Wisconsin for treating the rich lead ores of the



Figs. 4 and 5.—Carinthian Furnace, American Variety (Vertical and Horizontal Section).

Mississippi Valley, and still lingers in some places. A good description is given by Hofman.‡ The furnace employed is in both cases essentially the same, and the American variety (which is the simpler) is shown in plan and section in Figs. 4 and 5.

* Anthracite slack. † *Metallurgy of Lead*, 1870, pp. 261-271.
‡ *Metallurgy of Lead*, 1893, p. 89.

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The charge in this furnace was about 1500 lbs. of galena, which was worked off in twelve hours, extracting an unknown proportion of the lead present, and leaving a "grey slag" which contained 55 per cent. Pb, chiefly as oxide, but partly also as silicate and sulphate. The Carinthian furnace is now, practically speaking, extinct, except in a few isolated localities, having been replaced by other methods less costly for labour and less wasteful of fuel.

The English Method.—As already mentioned, the characteristics of this method are the use of large furnaces and moderately heavy charges, which are worked off quickly at a high temperature, the direct yield of lead being high and the volatilisation loss also rather high. Two main varieties of the method may be described according to the style of furnace employed—viz., the *Flintshire*, and the Spanish reverberatory furnace or "*boliche*."

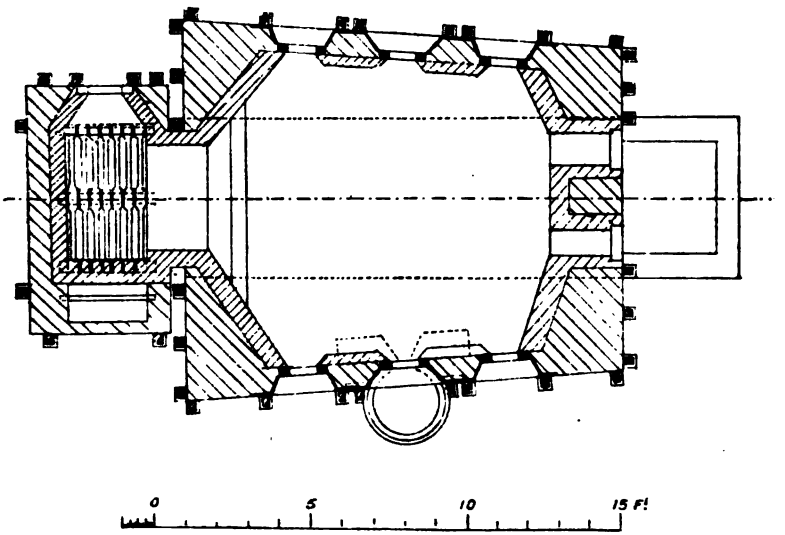

Fig. 6.—Flintshire Furnace.

The Flintshire Furnace.—The ordinary form of this furnace is built upon an air vault, which serves to cool the hearth. In some modified furnaces, instead of this vault, the whole furnace is open underneath, and is supported on iron rails or bars, and in any case it must be very strongly bound with cast-iron plates, buckstaves, and tie-rods. Common red brick is employed for all the outside work for the lower bottom, and for all parts of the furnace not exposed to a high heat, but the interior part of the furnace is built of firebrick. The true working bottom of the

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furnace varies from 6 to 12 inches in thickness, and is composed of the grey slag produced in the smelting process, about 5 tons being required for the formation of the bottom, which is patched as required with slags produced in the furnace itself. Fig. 6*

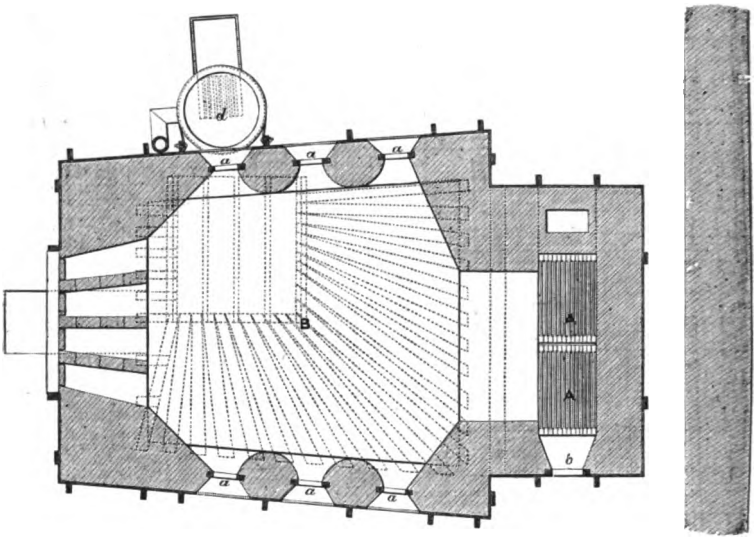

Fig. 7.—Smelting Furnace, Couëron; Horizontal Section on C.D.

shows the ordinary form of Flintshire furnace, in which the centres of the fireplace and flue are approximately in the longitudinal axis of the hearth, and the cast-iron lead well is situated in front of the middle working door at the front of the furnace. Figs. 7, 8, and 9† show Hutchison's modification introduced at Couëron, in which the line joining the grate and flue is set still further to one side of the longitudinal axis of the hearth, and the lead pot is placed in front of the third front door in order to withdraw the lead as far as possible from the influence of heat. This furnace also shows the construction on iron girders, instead of the usual "air vault"; but these details are, of course, not essential. The firebridge is always air cooled, and it will be noticed that the exit flue is divided so as to permit of the flame being more spread towards the back of the hearth (*i.e.*, the side opposite the well). The cast iron pot is usually provided with a separate fireplace in order to keep the lead molten while it is being ladled. The door frames and skew backs are of cast iron, $\frac{1}{2}$ inch thick.

* From Percy, *Metallurgy of Lead*, 1870, p. 225.
† From Phillips, *Elements of Metallurgy*, 1891, pp. 643, 644.

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Mode of Working.—The ores treated are from 75 to 80 per cent. by iron crucible assay. The usual charge is 21 cwts. dry

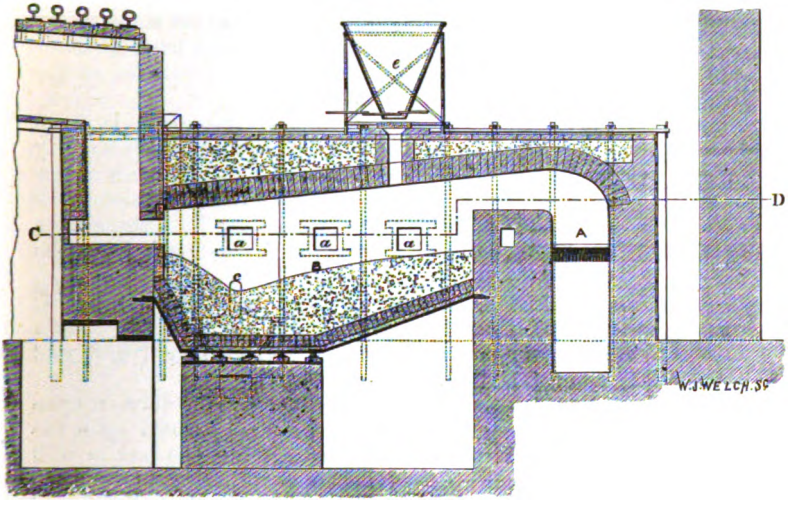

Fig. 8.—Smelting Furnace, Couëron ; Longitudinal Section.

weight (at Couëron, 27 cwts.), which, if not already fine enough, is crushed with rolls to about an 8-mesh ; after which it is

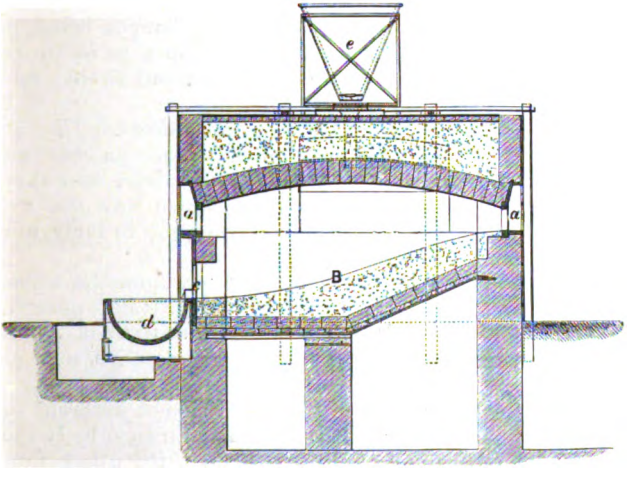

Fig. 9.—Smelting Furnace, Couëron ; Transverse Section through Tapping Hole.

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charged into the furnace, still at a red heat from the previous operation, and spread over the hearth.

First Stage—"Calcination."—The temperature is kept low, the damper being closed, and all the doors are left open so as to get as much oxidation as possible. This stage lasts from an hour and a half to two hours, by which time about one-third of the lead is oxidised—principally to PbO.

Second Stage—"Roasting" or Reaction.—The grate is freed from clinkers and fired up with coal, and the dampers are slightly opened, while the front doors are closed, and the charge is vigorously rabbled through the back doors. Effervescence takes place and much lead trickles down into the well. This stage lasts about half an hour, making a total of three hours from the charging.

Third Stage—Melting down.—The doors are closed, the damper opened and the fire urged so as to melt down the whole charge into the well. This stage lasts about half an hour (three and a half hours from charging).

Fourth Stage—Setting up.—All the doors being thrown open to cool the charge, a shovelful of slaked lime is thrown upon the surface of the molten slag in the well, while the bed is well scraped with iron paddles to detach any adhering half-melted portions of the charge. All such material detached is well mixed by rabbling with that pushed back from the lead-well after thickening with lime, and the whole is then raked back and "set up" on the sloping part of the hearth immediately beyond the firebridge. This stage takes about half an hour (four hours from charging).

Fifth Stage—Second Calcination.—The damper being partly closed, the two doors near the fire are left open so as to oxidise the charge again during another period of about twenty minutes (four hours twenty minutes from charging).

Sixth Stage—Second Roasting and Melting down.—The damper is fully opened and all the doors closed. Vigorous effervescence with reduction of metallic lead first takes place, and then the remainder of the charge quickly melts down into the well on top of the lead. This stage takes half an hour to forty minutes (five hours from charging).

Two shovelfuls of lime being now thrown upon the surface of the slag and well rabbled in to thicken it, the slag is pushed back from the taphole and the furnace tapped into the pot. The slag is raked out through the middle front door and a new charge dropped and spread.

The above sequence of operations is varied at different works; thus with somewhat poorer ores it is common to subject the slag to a second "setting up," followed by a third calcination and melting, the whole process then taking six hours actual working time, or nearly seven hours including raking out the slag, cleaning

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the hearth and spreading a fresh charge. Usually, however, two charges are readily worked off in a twelve-hour shift by two smelters and a labourer.

The lead in the pot is allowed to cool before ladling, during which a considerable quantity of dross (consisting mainly of PbS) separates, the separation being assisted by stirring in coal slack and hot cinders. The mixture of dross and slack is thrown back into the furnace-well, when a small quantity of lead immediately sweats out, and is allowed to run through the taphole before stopping this with a plug of mortar for the next charge (already spread and "calcining").

Analyses of Produce.—The following table adapted from Percy* shows the actual condition of the charge at different stages of the process :—

TABLE VII.—Composition of Charge at End of Various Stages.

Sample after :—	Ore charged.	First Stage. Calcination.	Third Stage. Melting.	Fourth Stage. Setting up.	Fifth Stage. Second Calcination.	Sixth Stage. Second Melting.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
PbS, . . .	89·95	63·82	53·32	24·76	4·35	0·90
$PbSO_4$, . .	...	3·42	4·78	6·94	14·02	9·85
PbO, . . .	5·15	27·25	31·49	43·12	47·50	48·87
ZnS, . . .	0·99	...	...	...	...	...
ZnO, . . .	...	1·25	3·00	5·02	5·72	7·52
CaO, . . .	0·65	1·32	2·14	7·38	11·51	12·68
$Fe_2O_3Al_2O_3$, .	0·42	0·88	1·54	2·95	4·25	5·87
Combined SiO_2, .	...	...	...	8·32	11·04	12·52
,, CO_2, .	1·62	...	...	...	...	...
Insoluble residue,	0·85	1·60	3·99	1·12	0·80	1·45
Total, . .	99·63	99·54	100·26	99·61	99·19	99·66
Total Pb, .	82·71	91·36	78·66	66·22	47·86	52·88
Approx. weight of charge, .	21 cwts.	18 cwts.	8 cwts.	4 cwts.	3½ cwts.	2¾ cwts.

It is noteworthy that the proportion of $PbSO_4$ at first formed is comparatively small, the lead being chiefly converted direct into oxide. The temperature of the mass at the first melting down is so low that no lead silicate is formed. After the addition of lime and the elimination of more lead, however, the

* *Op. cit.*, p. 235.

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residue (which is now much richer in ZnO, Al_2O_3, and Fe_2O_3, as well as CaO) is so much more infusible that, at the increased temperature to which it is now exposed, PbO and SiO_2 enter into combination with each other. Percy discusses at some length* the function performed by lime in the process, and comes to the conclusion that its action is essentially, if not exclusively, mechanical. While its principal function is undoubtedly mechanical, the author would suggest that possibly it may assist in liberating PbO from silicate formed during the first melting down, to act upon residual PbS; for, although the silicates of lead undoubtedly react upon PbS direct (as proved by Beck†), yet the temperature at which this reaction begins is in all probability above that which prevails at the second calcination stage of the lead smelting process. Similarly, Percy himself shows that at the temperature of the final melting down of grey slag there is no reaction between lead sulphate and silicate.

Seeing what a large excess of oxidised compounds is formed in the final stages of the process, it might be supposed that a better proportion of lead would be extracted by keeping the amount of oxidation low. It should be borne in mind, however, that besides the bad effect of a large quantity of PbS liquating out with the lead, a lessened oxidation at first would greatly increase the duration of the process, and, therefore, its cost; besides, in all probability, increasing the volatilisation losses, since PbS is much more volatile than either the metal or its oxide.

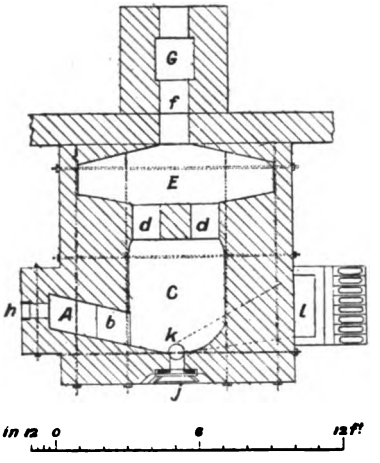

Fig. 10.—The "Boliche" Furnace.

At *Couëron* (France), until recently, rich galena ores from Sardinia were smelted in the modified Flintshire furnace (already figured). but the process was modified by lengthening its duration and lowering the temperature after the Silesian method, so that the charge was never allowed to melt. By these modifications in the furnace and in the process, the loss by volatilisation was reduced very considerably.

The "*Boliche*" *or Spanish* furnace, so widely used throughout

* *Op. cit.*, p. 237.

† Quoted by Percy, *op. cit.*, p. 48.

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the south of Spain, is shown in Fig. 10.* A is the fireplace adapted to burn brushwood, *b* the firebridge, C the smelting hearth more or less circular in form, *dd* the flues through which the gases escape into a second chamber, E, the function of which is said to be the checking and regulation of the draught, *f* the exit flue, and G the chimney. The fire door is at *h*, and the working door at *j*; in front of the latter is the well, *k*, to which the hearth slopes, and which communicates by means of an underground flue, shown in dotted lines, with the iron reservoir, *l*, from which the lead is ladled into moulds. The furnace is built entirely of refractory sandstone.

Of recent years furnaces of this general type have been adapted by the English companies operating at Linares so as to burn coal. This difference of fuel, besides requiring different form and dimensions of the firebox, has rendered it necessary to lengthen and narrow the working hearth. Further details as to the working of these improved "boliches" (which may be regarded as working on the English principle, though, unlike the present Silesian furnaces, they originated independently in Spain, and were not merely improved from an old English model) are given in Table IX.

In the old "boliche" burning brushwood, ashes and fine cinders from the ashpit were exclusively used for the purpose of "drying" the charge and allowing it to be "set up" for re-roasting. With the advent of English smelters, lime was substituted; but the present management of the Linares works has found it advantageous to revert to the use of fine cinders to the amount of one-fifth of the lime. The Linares works are quite important, since in 1895 they treated 11,169 tons of ore, yielding 7406 tons of ore-lead with 12½ ozs. Ag per ton, and 650 tons slag-lead with 4 ozs. Ag per ton.

The Silesian Process may be considered as the slow, low temperature Carinthian process carried on with large charges in a modified English furnace, the final stage of slag reduction being omitted and carried on in cupolas. The use of a large furnace secures the principal advantages of the English process—namely, a large production at low cost for fuel and wages. The incomplete slag reduction is no drawback, since in any case reverberatory treatment of lead slags has always to be supplemented by a separate treatment in a hearth or cupola, by which means the volatilisation loss is lessened; and by stopping the reduction early no copper or antimony come down with the last lead to contaminate that already tapped. The lead produced in this process is, therefore, purer than in the English process. Moreover, the volatilisation loss of lead is less than by any other process, owing to the low temperature at which the roasting is conducted.

* From Percy, *op. cit.*, p. 250.

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Silesian Process at Tarnowitz (Upper Silesia).*—The process at the Friedrichshütte, Tarnowitz, is a little peculiar in that a portion of the ore, specially rich in blende, is roasted as thoroughly as possible in a long reverberatory roaster and then added to the rest of the charge in the lead furnace, together with flue dust, litharge, and other oxidised products from the refinery, all of which assist in the reaction upon undecomposed lead sulphide.

The ores treated contain about 70 per cent. lead as galena, with 5 per cent. zinc as blende and trifling admixtures of pyrites, chalybite, calcite, dolomite, and calamine. They are practically free from copper and arsenic, contain very little antimony, and only about 5 ozs. of silver per ton.

The construction of the furnace used is shown in the following Figs. 11 to 14. In general form it somewhat resembles the English furnaces already described, especially the Couëron modification of the Flintshire furnace, for the hearth slopes gradually towards the sump, and not suddenly as in the old Flintshire furnace, and the well is at the farther end door. It is rectangular in form, with 4 working doors on each side, the well being at the coolest end of the furnace below the door next the flue, the opening into which is divided into 4 by means of brick partitions. The bridge is hollow, and contains a cast-iron trough, cooled by a current of air which is drawn through it by means of a hole in the roof, as shown on the plan, Fig. 12. The iron-grate bars are placed transversely in the firebox, and not longitudinally as usual, firing takes place from both sides, ashes being removed at the end of the furnace. The roof is horizontal from the firebox to the centre of the hearth, where the charging opening is situated, falling thence in a straight line to the flue (longitudinal section, Fig. 11). The furnace is completely cased in iron plates strongly bound by iron-rail buckstays and tie-rods. The hearth is built of red brick on a thick sand bed sloping towards the flue at about the right angle for the final hearth, as shown in Fig. 13. Over this is formed the trough-like brasque bottom, composed of clay 1 part, coke 3 parts, which slopes towards the well, and varies in thickness from 4 inches to 12 inches. The actual working bottom is a layer 4 inches thick of slag having a high melting point, and spread evenly over the whole area, following the surface of the brasque bottom already rammed to the proper curve. This working hearth used to be made of tap cinder, but ordinary gray slag mixed with lime is now used instead, exactly as in English furnaces.

Mode of Working.—The charge weighing 2500 kilos. (say 2½ tons English), and crushed to pass a 5-mesh screen, is dropped into the furnace, which is already at a dark red heat (500° to 600° C.),

* *Zeitschrift für Berg-Hütten.- und Salinen-Wesen*, vol. xxxii., p. 94, and vol. xxxiv., p. 292; also Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 305.

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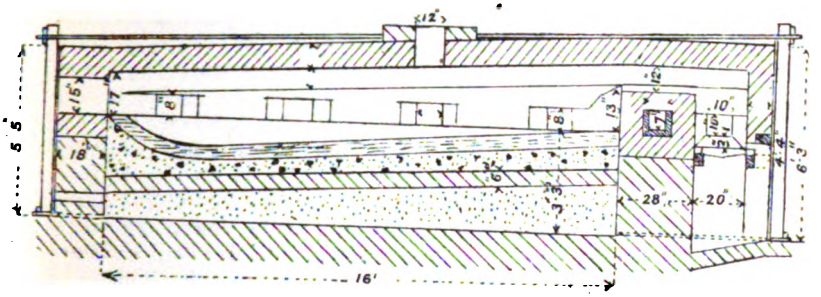

Fig. 11.—Silesian Furnace (Longitudinal Section).

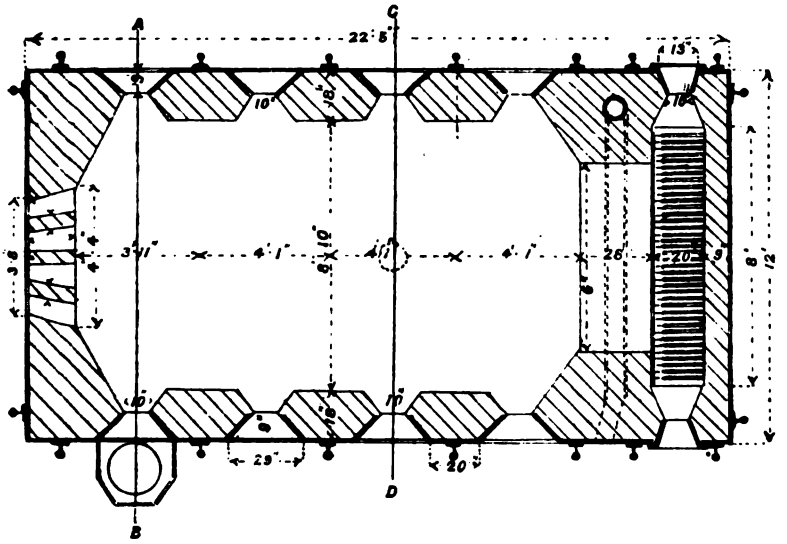

Fig. 12.—Silesian Furnace (Plan).

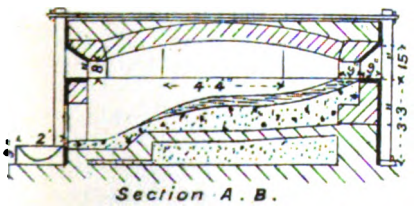

Fig. 13.—Silesian Furnace.

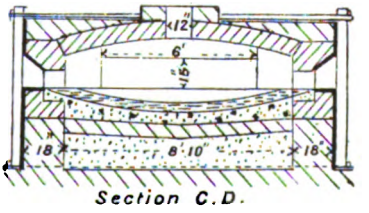

Fig. 14.—Silesian Furnace.

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and spread out so as to form a layer 3 inches to 4 inches thick. The fire is fed with cinders only, so as to keep the temperature low; the galena begins to decrepitate, and the charge gradually acquires the temperature of the furnace after about an hour. The doors are now opened, and roasting begins at the surface of the charge, a white crust of oxide and sulphate being formed. About every twenty minutes the charge is turned over by means of paddles, or stirred with rabbles, so as to expose new surfaces to the action of the air and prevent clotting. After four hours the oxidised additions are made, consisting of a portion of the same ore previously roasted, with flue dust and carbonate ore when available. The total weight of these additions is about 10 to 12 cwts., and they are well stirred in; at the same time the grates are cleaned and fed with good coal, and the damper is fully opened so as to raise the temperature. The reaction period begins, lead runs down, and the ore softens so much as the temperature rises that lime has to be thrown on the charge and well rabbled in to stiffen it, after which the whole charge is turned over. The working doors being open during these operations, the furnace cools off so much that the flow of lead ceases, while more of the undecomposed sulphide oxidises. On shutting the furnace doors the temperature soon rises, reaction begins again and more lead flows out. This alternate oxidation and heating of the charge takes place at intervals of about one and a-half to two hours throughout the whole period of reaction. About three hours from the start the well is tapped into the kettle, poled there, drossed, and ladled into moulds, the dross being set aside for subsequent treatment. This first kettleful of "virgin lead" carries from 50 to 60 ozs. of silver per ton. About 10 cwts. of oxidised skimmings from the steam refining of lead desilverised by the Parkes process, and containing 75 to 80 per cent. PbO and 18 to 20 per cent. ZnO, are now added and the doors closed, while the fire is fed with small coal to ensure a smoky flame. This reduces lead sulphate to sulphide, and lead oxide to metal, and the flow of lead begins again. Further tappings are obtained each hour and a-half, steadily decreasing, however, in amount and in silver contents. Before the last tapping the kettle drosses obtained by poling the previous kettle leads are thrown into the furnace and melted down with the last tapping. In all, the reaction period lasts seven hours; after which the residues are raked out, the hearth repaired where necessary and sprinkled with lime, and a new charge added.

The removal of the residues was formerly effected by raking them out of the last working door opposite the well into a box filled with water, but the fumes were very injurious to the workmen employed, and dangerous explosions sometimes occurred. In the latest furnace, the residues are raked through an

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opening in the furnace hearth, which is covered by an iron plate during the working of the charge, into a wheeled iron slag pot underneath. This improvement, not shown in the figure, has had a great effect on the health of the workmen.

About 60 to 65 per cent. only of the lead contents of the ores are extracted as work-lead, containing on the average 6 to 7 ozs. silver per ton; the remainder is all found in the residues (amounting to 30 to 35 per cent. of the weight of the charge and containing 40 to 55 per cent. metal), except about 4·45 per cent. Of this, most is recovered in the form of flue-dust, which chiefly consists of $PbSO_4$, so that the real *loss* in the process unaccounted for is only $1\frac{1}{2}$ per cent.*—calculated on the commercial dry assay of the ore. The residues are treated in a cupola furnace.

The total length of an operation is eleven to twelve hours, 2 men working on each 12-hour shift. The consumption of fuel varies between 40 and 50 per cent. of the weight of the charge, and that of lime amounts to about 1 per cent.

At *Bleiberg near Montzen* (Belgium)† the furnace in use is similar, except that it has a fireplace at each end, the flue opening being in the middle of the arch. The calcination period on a 2-ton charge lasts six hours, and the period of reactions six hours. Further details are given in Tables VIII. and IX.

The Flowing or Cornish Process.—In this process, now extinct, the operations of calcination and of reaction were performed in separate furnaces, and a larger quantity of PbO and $PbSO_4$ was formed in the first than was required for reaction upon PbS in the second. The hearth of the calcining furnace was rhomb-shaped, the firebridge and flue door being at the ends of the longer axis, and the working doors at the ends of the transverse axis. The charge was from $1\frac{1}{2}$ to 3 tons, according to size, and the calcination took fifteen to eighteen hours with a coal consumption of 30 per cent. by weight.

The flowing furnace is rectangular and longer, and contains four working doors on opposite sides, besides the flue door at the end opposite the firebridge. The hearth is saucer-shaped in longitudinal section and wholly inclined sideways towards the second door on the front, beneath which is the usual cast-iron pot. The whole of the hearth is carried on iron bars stretched transversely across the foundation walls and arranged roughly parallel to the contour of the working bottom.

The charge in the Cornish process was 2 tons of calcined ore, which was spread on the hearth and run down into the well in about three hours, when the lead was tapped out, the residues thickened with lime and cut in and "set up." Some 5 per cent. of scrap iron was then thrown into the well, and the charge

* Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 307.
† Schnabel, *op. cit.*, p. 308.

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again melted down, the lead being tapped out together with the matte, or "slurry," formed, which carried nearly all the copper present in the ores. The whole time required to work off a charge was about eight hours, and the coal consumption 40 per cent. The slags were usually poor enough to throw away and the process was specially adapted to the smelting of coppery ores containing only 60 to 70 per cent. lead.

The whole operation in the flowing furnace usually took about eight hours, and on account of the higher temperature required to melt the larger quantity of refractory material, the volatilisation loss and consumption of fuel were both greater than in the Flintshire furnace, which more than offset the advantage of cleaner slags. The flowing furnace has been, however, very largely used in Wales and elsewhere for reducing the grey slags of the Flintshire furnace, as well as for treating rich silver ores, lead residues, jeweller's "sweep," &c., and is still in use to a considerable extent for such and similar purposes.

TABLE VIII.—Details of Reverberatory Lead Furnaces.

	Carinthian Method.		English Method.			Silesian Method.	
	Raibl, Carinthia.	Granby, Missouri.	Holywell, Flintshire.	Couëron, France.	Tarnowitz, Silesia.	Tarnowitz, Silesia.	Montzen, Belgium.
Reference, . .	1.	2.	3.	4.	5.	6.	7.
Hearth length, . .	11′ 0″	10′ 0″	12′ 0″	...	11′ 9″	16′ 0″	15′ 5″
,, width at bridge, .	5′ 0″	2′ 6″	3′ 6″	...	10′ 10″	8′ 10″	9′ 6″
,, ,, flue, .		4′ 0″	4′ 0″				
,, medium width, .		2′ 0″	9′ 6″				
Grate length, . . .	7′ 0″	3′ 0″	4′ 6″	...	8′ 0″	8′ 0″	6′ 6″
,, width, . . .	1′ 3″	2′ 0″	2′ 6″	...	1′ 8″	1′ 8″	2′ 8″
Bridge length, . .	3′ 7″	2′ 0″	3′ 6″	...	6′ 0″	6′ 0″	6′ 0″
,, height above hearth,	4″-5″	...	12″	...	1′ 3″	1′ 3″	...
,, height to roof, .	9″	6″	9″	...	1′ 0″	1′ 0″	1′ 0″
Grate area : hearth area, .	1 : 6	1 : 5·4	1 : 10	...	1 : 9·6	1 : 10·6	1 : 8·3
,, : chimney section, ...	7 : 1	8 : 1	1·1 : 1	...	...	...	...
Hearth area (square feet),	55	31	94·5	...	127	140	141

Comparison of the Various Processes.—Comparative data have been thrown into tabular form to facilitate reference. Table VIII. gives constructional details of various lead furnaces, and Table IX. details of the operations carried out in them.

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TABLE IX.—Comparative Data of Reverberatory Lead Smelting.

	Carinthian Method.		Flintshire Method.			Boliche.	Silesian Method.	
	Raibl, Carinthia.	Granby, Missouri.	Holywell, Flintshire.	Couëron, Loire Infer.	Tarnowitz old furnace.	Linares.	Tarnowitz new furnace.	Montzen, Belgium.
Reference,	1.	2.	3.	4.	5.	6.	7.	8.
Charge—weight in lbs.,	370-430	1500	2352	2970	4400	3526	6820	4580
,, lbs. per square foot of hearth,	7-8	48	25	...	35	196	49	32·5
,, assay lead, per cent.,	70	...	77½	81	73	77	70	80
,, silver, ozs. per ton,	...	...	...	...	24·4	...	...	...
Duration of operation, hours,	10-12	9-11	5½	9½	7	8	12	16
Men per furnace, 24 hours,	1½	2	6	...	6	...	4	...
Lead produced per charge, lbs.,	230-270	...	1575	...	2807	...	...	2308
Grey slag produced per charge, lbs.,	95	...	308	638	700	809	1700-2300	1456
,, per cent. of charge by weight,	24	...	13·1	21·5	16	23	25-35	33
,, assay lead, per cent.,	4	55	55·5	50	38·8	21	45-46	66
Flue dust per charge,	...	...	...	...	121 lbs.	164 lbs.	...	...
,, per cent. of charge by weight,	...	...	...	...	2·75	4·7	...	...
,, assay lead, per cent.,	...	...	...	...	50	45	61	...
Of lead charged :—								
Obtained in bars, per cent.,	93	...	87·0	82·4	87·4	86·0	60-65	66·1
,, from grey slag, per cent.,	...	...	7·0	12·4	8·0	5·6	30-35	27·8
,, from flue dust, per cent.,	...	...	1·0	5·2	1·4	2·4	2-3	5·1
Volatilisation—loss, per cent.,	7*	...	5·0		3·2	6·0	1½-2	
Fuel consumption—coal, per cent.,	...	...	50·0	40·0	...	...	40-50	40·0
Consumption of lime, per cent.,	...	...	...	2·0	1·0	4·0	1	...
Cost of smelting—per ton :—								
Superintendence, &c.,	...	...	...	...	...	0 : 9	...	...
Labour,	...	...	...	...	...	3 : 4	...	...
Coal,	...	...	...	...	...	7 : 9½	...	...
Lime,	...	...	...	...	...	0 : 4½	...	...
Tools and general expenses,	...	...	...	...	...	4 : 7¼	...	...
Total,			9 : 6		9 : 0	16 : 10		

* Total losses.

References.—1. Hofman, *Met. of Lead*, 1893, p. 107. 3. Percy, *Met. of Lead*, 1870, p. 231. 4. Phillips, *Elements of Metallurgy*, 1879, p. 540. 5. Percy, *op. cit.*, p. 243, and Hofman, *op. cit.*, p. 107. 6. *Private Communication*, H. W. Pearse, 1896. 7. Schnabel, *Handbuch der Metallhüttenkunde*, 1894, p. 305. 8. *Ibid*, p. 308.

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Bye-Products and their Treatment.

The principal bye-products of reverberatory lead smelting are grey slag and fume.

Grey Slag.—The composition of this substance varies considerably, as shown by the following analyses:—

TABLE X.—Analyses of Grey Slags.

	Carinthian Furnace, Engir.	Air Furnace, Missouri.	Flintshire, Holywell.	Flintshire, Bagillt.	Silesian, Tarnowitz.
Reference,	1.	2.	3.	4.	5.
Pb (free),	...	...	...	...	..
PbS,	...	20·929	0·90	...	...
$PbSO_4$,	...	2·349	9·85	18·73	13·269
$PbSiO_3$,	45·05	44·261	59·28	48·28	12·373
PbO,	...	...	2·11	...	24·375
ZnO,	20·80	7·146	7·52	12·00	22·857
Al_2O_3,	14·70	0·152	3 01	0·71	tr.
Fe_2O_3,		3·680	2·86	...	...
FeO,	...	...	...	3·89	8·957
FeS,	...	...	...	...	1·823
MnO,	...	...	...	...	tr.
CaO,	3·70	4·650	12·68	13·50	11·190
MgO,	...	3·948	...	...	...
C,	...	...	...	...	4·821
Ag,	...	...	...	...	0·015
S,	0·10	...	...	...	...
SiO_2,	15 85	12·049	...	2·12	...
Insoluble,	...	...	1·45	...	...
	99·80	99·063	99·66	99·23	99·680
Total Pb,	...	...	52·88	...	...

References.—1. Bouhy, "La fabrication du plomb," 1870. 2. Williams, *Geol. Survey of Missouri*, 1877, pp. 8-101. 3. Percy, *Metallurgy of Lead*, 1870, p. 235. 4. *Ibid.*, p. 239. 5. *Ibid.*, p. 242.

It is sometimes treated in the flowing furnace, sometimes in the slag hearth (a form of low, open, blast furnace), more commonly, however, in some form of cupola or high blast furnace.

Fume.—Some analyses of this substance from reverberatory furnaces are given in Chapter xii., and the various methods of collection and condensation are also dealt with in that chapter. Various modes of "bricking" it, as a preparation for further treatment, are referred to in Chapter x. At a large number of reverberatory smelting works the fume is

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bricked and run down in a cupola together with the grey slag, but, owing to its light character, it is best treated in reverberatories.

At Linares* the bricked fume is first smelted together with some fine coal in a reverberatory, yielding a considerable proportion of lead and a very rich lead slag called "black slag," which is found to assist materially in smelting the grey slags from the modernised "boliche" or Spanish form of the English reverberatory. These grey slags contain 21 per cent. Pb, and are smelted together with the above "black slag," a certain proportion of crude fume, and of iron flux in a round sandstone "Castilian furnace" with 5 tuyeres, using coke fuel, the blast for which is supplied by a fan. The total quantity of charge put through in twenty-four hours is—grey slag 20 tons (metric), black slag 9 tons, fume 9 tons, iron flux 6 tons, which is smelted with 8 tons coke. It is reckoned that in this slag and fume smelting 15 per cent. of the lead charged into the furnace goes back to the flues. During 1895, 2570 tons of grey slags and 520 tons fume were treated with a yield of 650 tons slag- and fume-lead.

The fume-condensing arrangements at these works are referred to in Chap. xii.

Suggested Improvements in the Roast Reaction Process.—As already seen, the ordinary reaction process in reverberatories is only adapted to the treatment of high grade galena concentrates containing, say, 60 per cent. lead or upwards; with those of lower grade the process is much lengthened, and the final slags retain too large a proportion of the total lead contents of the charge. The bulk of low quality zincy concentrates and middlings, therefore, are either reconcentrated (at a ruinous loss) in order to bring them up to a higher grade, or else are treated in blast furnaces after roasting, as is done (for example) with all the second quality concentrates and the zincy slimes of the various dressing works at Broken Hill, N. S. W.

The small capacity of existing reverberatory lead furnaces and their heavy cost for fuel and labour render them very unsuitable to the treatment of zincy galena containing, say, 50 per cent. lead, while the very high cost of coke as compared with slack coal and the fine condition of the materials are great drawbacks to the use of the blast furnace. In a paper read before the Australasian Institute of Mining Engineers in April, 1897,† the author suggested that a roast-reaction method carried out in two separate stages in furnaces of large capacity, the red hot ore from the roaster being charged direct into the smelting furnace upon a bath of molten lead, would combine the advantages of the reverberatory (use of cheap raw fuel) with those of the blast

* *Private communication*, H. W. Pearse, Sept., 1896.

† *Transactions Austral. Inst. M. E.*, vol. iv., 1897, p. 124.

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furnace (large capacity, &c.). For details the original paper may be consulted, but the following summary may be given here:—

It is suggested that three-fifths (more or less as shown by assays) of the material to be treated should be roasted in a long hearth reverberatory, say, 50 feet by 16 feet, at a fairly high temperature with low draught, so as to convert as much as possible of the lead into $PbSO_4$. The hot roasted ore, drawn into hopper trucks, should then be charged, together with an equivalent quantity of raw ore, into the hoppers of a large reverberatory smelting furnace.

This should be, say, 24 feet long by 10 to 12 feet wide, supplied with heated air under the grate, like those used for copper smelting at Butte,* Montana, but, unlike them, built into a wrought-iron tank and provided with a water jacket round the sides, after the fashion of a softening furnace.† It would have its taphole or well at least 6 inches or more from the bottom so as to contain a pool of 40 or 50 tons of molten lead to assist in spreading and quickly heating the charge, and such a furnace would probably be capable of working off a 5-ton charge in two hours or less with a coal consumption of 15 to 18 per cent. The slag would be skimmed from 3 doors near the flue end, as in a copper furnace, and the lead could be tapped as required from a taphole, or "dipped" continuously from a "syphon tap" lead well,‡ as from a blast furnace.

Including that used in roasting the larger part of the charge, the total consumption of coal would probably not exceed 30 per cent. in all, as against 40 to 50 per cent. in the ordinary English process treating a less refractory ore; and, although the grey slag would have to be re-smelted, its amount would not be so much greater than that produced in the Flintshire furnace as to offset the saving in the first smelting, even allowing for a somewhat increased volatilisation loss, against which might be set the much smaller labour cost. As compared with blast furnace smelting, the saving in dear coke would more than compensate for the increased amount of cheap slack coal used, and the treatment of other ores in the blast furnace, together with the grey slags, would be much facilitated by getting rid of the fine concentrates.

* *v.* Peters, *Modern Copper Smelting*, 7th Ed., 1895, pp. 452 to 465.
† *v.* Figures and description, chap. xv.
‡ *v.* Chap. viii., p. 139.

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CHAPTER V.

LEAD SMELTING IN HEARTHS.

THE "hearth" is a species of low furnace, of which the blacksmith's forge is the simplest type, in which the charge mixed, or in actual contact, with fuel is handled by appropriate tools, while the heat is kept up by the action of a blast on the fuel. It may be said, therefore, to be in its operation intermediate between a reverberatory and a blast furnace. The mixture of fuel and ore floats on a bath of molten lead, of which the hearth is kept full so as to avoid the formation of crusts. The "roast and reaction method," as carried on in these furnaces, differs essentially from that in reverberatories because roasting and reaction go on simultaneously, and there is considerable direct reduction of lead oxide (formed by the action of the blast on galena) to metal by the glowing fuel. As regards purity of the ore adapted to the process, the same conditions which govern its applicability to reverberatory treatment must be even more strictly observed, while the volatilisation loss being much higher, argentiferous galenas are always better treated in reverberatories. Finely-powdered ore, moreover, cannot be treated in a hearth without previous agglomeration, as it would be blown away by the blast. The capacity of the hearth is less than that of the reverberatory, and it requires power and a blower. On the other hand, the fuel consumption is less (usually not more than one-half, any kind of fuel can be used from coal to wood or peat), and it possesses the great advantage over a reverberatory of being easily stopped and started again without much loss of time or of heat and without those strains caused by alternate expansion and contraction which are so destructive to the brickwork of a reverberatory. In spite of arrangements for drawing off and condensing as much as possible of the volatilised lead fume, the large amount which escapes is very unwholesome to the men employed, who are more exposed than those working reverberatory furnaces.

The hearth is invariably made of cast iron, and in front of it is a cast-iron "workplate," with a groove to carry off the reduced lead into a kettle. There is usually a partial front wall composed of a thick bar of iron, but often the front is simply a dam formed of ashes and powdered galena which is impervious to melted lead. The sides and back may be cooled simply by radiation from large and heavy castings (Scotch hearth), by a current of air (Rossie hearth), by a water-box (American hearth), or by both air- and water-boxes combined (Moffet-Jumbo hearth).

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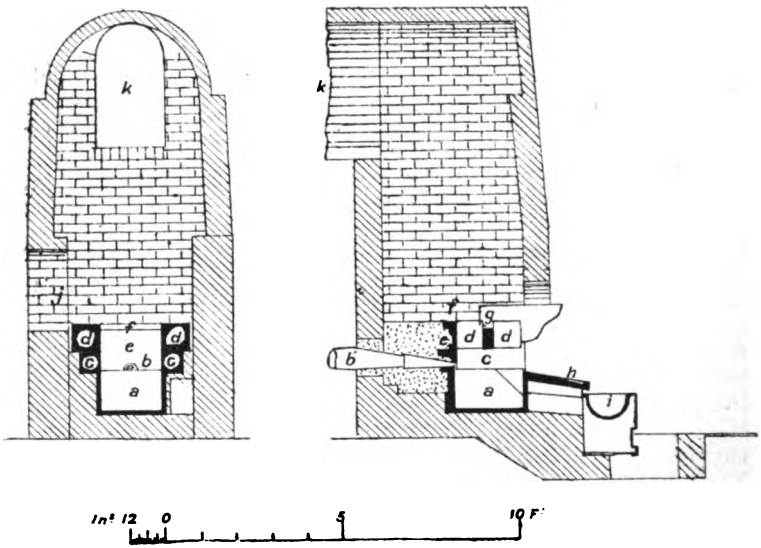
These differences may conveniently be taken as representing four distinct modifications of the hearth process, though the manipulation is much the same in all.

1. **The Scotch Hearth.**—This furnace was invented many centuries ago in the Leadhills (Scotland), where it is still in use, the principal improvements being the substitution of heavy castings for the flagstones and thin castings originally used to form the sides and back of the furnace, by which means the working of the furnace, formerly intermittent with periods of "cooling-off" in order to protect the furnace from destruction, can now be carried on continuously from Monday till Saturday. The fuel employed was formerly peat, but coal is now almost exclusively used.



Figs. 15 and 16.—Keld Head Ore Hearth.

Construction.—The construction of an ore hearth will be understood from the following Figs. 15 to 19. Figs. 15 and 16* represent the ore hearth of the Keld Head Co., Yorkshire, and Figs. 17 to 19 † that in use at Leadhills, which may, perhaps, be regarded as the typical form of Scotch hearth. The lettering in both series of figures is the same to facilitate reference. The base is formed of a cast-iron "hearth bottom" or "hearth box," *a*, cast in one piece; its dimensions are, at Keld Head, 23 ins. long, 21 ins. wide, and 12 ins. deep, the iron being 1½ ins. thick

* Percy, *Metallurgy of Lead*, p. 281.
† Sexton, *E. and M. J.*, Feb. 23rd, 1895.

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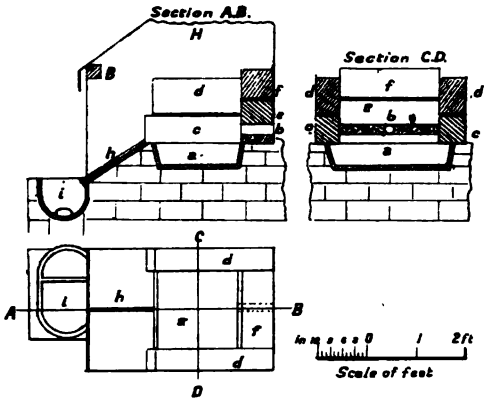
in front and 2½ ins. at the back; at Leadhills the box is 22 ins. long from front to back, 30 ins. wide and only 6 ins. deep, the iron being 1 in. thick throughout. This hearth bottom forms the crucible of the furnace, and, when running, is always full of molten lead. The hearth proper, in which the smelting takes place, is built upon it by means of heavy blocks of cast-iron, technically called "stones." In front of the hearth is the "workstone," *h*, which may be cast in one piece with the hearth bottom, as at Keld Head, but is more commonly a separate



Figs. 17-19.—Scotch Hearth as used at Leadhills.

casting. At the back is a single tuyere, *b*, which is bedded in a mixture of mortar and slag. The remaining pieces forming the hearth are as follows:—

cc. Two "bearers" or "lower sidestones" resting on the hearth box and measuring, at Keld Head, 2 ft. long × 7 ins. square (at Leadhills, 2 ft. 9 ins. long × 6 ins. square).

dd. Four keystones 10 ins. cube (Keld Head), or two "upper sidestones" 2 ft. 6 ins. long × 6 ins. wide × 10 ins. high (Leadhills).

e. "Lower backstone" or "pipestone," 2 ft. 6 ins. × 1 ft. 2 ins. × 3 ins. thick at Keld Head; and 2 ft. long × 8 ins. square at Leadhills.

f. "Upper backstone," 2 ft. 8 ins. long × 5 ins. wide × 2 ins. deep at Keld Head; 2 ft. long × 8 ins. square at Leadhills.

g. "Forestone," which at Keld Head is a block fitting between the two keystones and at Leadhills is absent.

In the figures the lead pot is shown at *i*, that at Leadhills having a transverse partition perforated at the bottom to allow scum, ashes, &c., to float on the surface of the lead in the larger division, while only clean lead flows under into the smaller division, from which it is ladled at intervals. The hearths at

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Keld Head are arranged under brick hoods as shown, *k* being a working door at the side through which fuel is charged, and *l* the connection with the main flue. At Leadhills a sheet-iron hood, H, supported on an iron crossbar, B, and a brick back wall carries off the fumes.

Mode of Working.—Each furnace requires two men on a shift, the shifts being formerly of eight hours, but now very commonly of six hours only; the tools used are paddles, shovels, and rakes; piles of ore, coal, and lime are arranged close in front of the hearth. After lighting a wood fire in the sump, coal is added under a light blast, continually turned over, and the ashes removed till the hearth is full of glowing fuel. A charge of about 20 lbs. of ore is then scattered on the bed of fuel, where it soon commences to yield lead and to slag. The bed of fuel is then lifted and stirred, the half-melted masses called "browse" are drawn out on to the workstone and broken up with the bar, completely slagged portions being thrown aside, while partially decomposed portions are returned together with more ore, and this process continued until the hearth becomes full of melted lead, upon which float the remaining fuel and half-decomposed residues. The hearth, being now in normal working order, receives new charges at intervals of about five minutes. Each charge consists of a shovelful of coal, which is sprinkled over the residues and thrown chiefly towards the back of the hearth near the tuyere, followed by from 20 to 30 lbs. of ore previously mixed with from $1\frac{1}{2}$ to 2 per cent. of lime. After adding each charge the fire is left undisturbed for about three minutes, one of the furnacemen then inserts his bar into the lead and raises the crusts lying beneath the fuel, while his companion with a long-handled shovel draws them out upon the workstone. The half-fused masses are broken up, slag is thrown into a water box at one side, while the half-decomposed ore is returned to the furnace with a little lime. The tuyere is cleaned out if necessary, a shovelful of coal added, and followed by another charge of ore.

The ores treated are pure galenas dressed by jig and buddle up to about 77 per cent. lead, and the lead is very pure, seldom requiring to be poled before ladling, though this is sometimes done to improve the quality. Each hearth treats $6\frac{1}{2}$ to 7 tons of ore per twenty-four hours, yielding about 4 tons (80 pigs) of lead, and the consumption of fuel is about 18 cwts. to 1 ton of coal slack, or say 10 to 12 per cent. of the weight of ore treated.

The grey slag produced is broken up and hand picked to remove pieces of lead and of half-decomposed ore, but still retains many small shots of metal. After separating these, a sample of Leadhills slag yielded on analysis* PbS 5·63 per cent., $PbSO_4$ 10·36 per cent., PbO 34·88 per cent. (equal to total com-

* *E. and M. J.*, Feb. 23, 1895.

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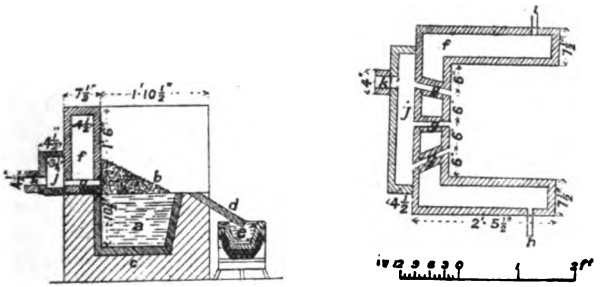
bined lead 34·8 per cent.), CaO 4·10 per cent., ZnO 0·95 per cent., Fe_2O_3 and Al_2O_3 18·20 per cent., SiO_2 26·00 = 100·12. It is allowed to accumulate till a sufficient quantity is obtained for a campaign, and is then run through a slag hearth. The fume drawn off through the hood by means of the draught caused by a high chimney is condensed—usually in chambers filled with brushwood through which a spray of water is continually falling. The water is led into a system of tanks, where it deposits a fine grey sludge which is plastered on the work plate to dry, and is then mixed with the ore charge in small proportions.

2. **The Air-cooled or Rossie Hearth.**—In this form of hearth, first introduced at Rossie, N.Y., and afterwards in the Mississippi Valley and at Bleiberg, the back and sides were cooled by circulation of the blast through the hollow castings of which they were formed. The capacity of this hearth was somewhat greater than that of the simple Scotch hearth, but the hot blast caused a greatly increased volatilisation loss, and on this account it has entirely dropped out of use.

3 **The Water-cooled Hearth.***—This is of American origin, and its construction is seen in Figs. 20 and 21. The hearth box,



Figs. 20 and 21.—Water-cooled Hearth.

a, filled with molten lead, upon which floats the charge of ore and charcoal, *b*, is of cast iron set in brickwork, *c*, and its capacity is about 2500 lbs. of lead. The workstone, *d*, is a separate casting with a groove leading to the kettle, *e*. Above the hearth box is the water box or "tuyere plate," *f*, of cast iron 1½ inches thick, which forms the back and sides of the hearth, and in which three tuyere holes, *g*, are cast. The water enters at *h*, and leaves at *i*. At the back is the wind box, *j*, into which the blast enters at *k*, passing into the furnace through three wrought-iron tuyere nozzles from 1 to 1½ inches diameter inserted

* Broadhead, *Geol. Survey of Missouri*, 1873-74, p. 492; Williams, Industrial Report, *Ibid.*, 1877, p. 36; also *Trans. A.I.M.E.*, vol. v., p. 324.

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in the tuyere holes. The tuyere level is from 1 to 3 inches above the constant level of the molten lead. Above the hearth is placed a sheet-iron hood (not shown) to carry off the fumes. Wood or charcoal may be used as fuel, but charcoal is more usually employed, and the capacity of each furnace is 4½ short tons (= 4 tons English) per twenty-four hours. These hearths are in common use in Missouri for treating the pure non-argentiferous galena of that region, the average composition of which is PbS 97·05 per cent., ZnS 1·41 per cent., FeS_2 0·34 per cent., insoluble 0 61 per cent.. Ag 1½ ozs. per ton. It is not easy to see, however, in what way they are superior to the Scotch hearths built up of heavy castings cooled by radiation, except in being somewhat cooler for the men to work at. The capacity is no greater, and, on the other hand, the cost of replacement of the iron water-back made in one piece through cracking and wear and tear is probably much greater over a series of years than that of the heavy Scotch castings, which are reversible as they become burnt, and have four wearing faces. The scarcity and cost of water would also be a difficulty, and an objection in many cases. The total weight of the Scotch hearth is considerable, but the pieces composing it are, with the exception of the hearth bottom, very portable, and for transport in mountainous districts the latter might be, if necessary, made of wrought iron reinforced at the front and back with replaceable cast-iron plates to resist burning.

4. **The Jumbo, Double, or Moffet Hearth.***—This hearth, designed by Moffet, is in use at the works of the Picher Lead Company at Joplin, Mo., and its construction is shown in Figs. 22 to 25. The hearth box is not set in brickwork, but consists of a simple iron trough 4 feet long, 3 feet 6 inches wide, and 10 inches deep, divided longitudinally by a hollow partition, and supported 26 inches above the floor by means of four short cast-iron pillars, so as to cool the lead by the circulation of air underneath. Upon each long side of the trough stands a water box 6 inches wide and 20 inches high, while on each end is placed an air box 4 feet 4 inches long, 6 inches wide, and 20 inches high. The hollow partition in the centre is also carried up 20 inches high by means of a pair of long hollow boxes, each 4 feet by 7 inches wide by 10 inches high. The upper one is the air box, and is partitioned longitudinally, each half being connected with the air box forming one end of the hearth through which the blast passes before entering the central air box. From each half of the latter seven copper tuyeres, each of 1 inch inside diameter, descend through the water box and deliver the blast at the level of the top of the hearth trough. The furnace thus consists of two long hearths placed back to back, water cooled in their hottest part, and air cooled above,

* Dewey, *Trans. A.I.M.E.*, vol. xviii., p. 674.

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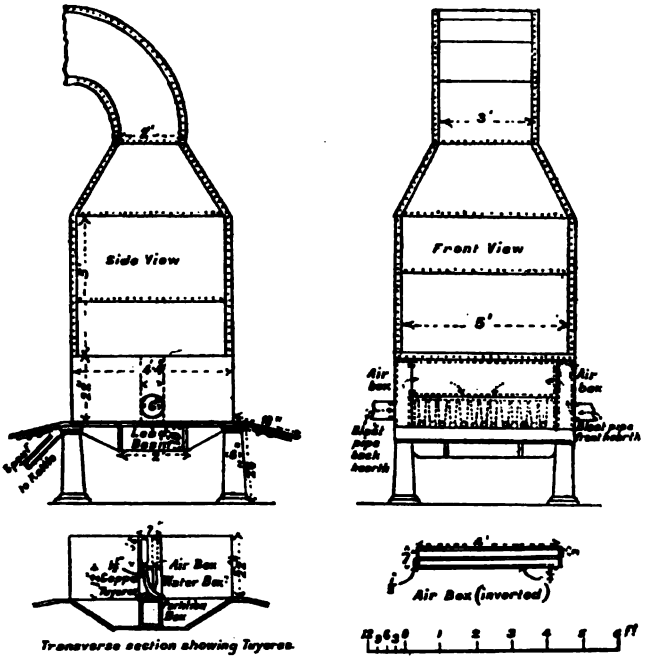
provided with a hot blast so as to volatilise a large proportion of the lead, and delivering their fumes into a common sheet-iron hood 5 feet by 4½ feet by 11 feet high, which is connected with flues and dust chambers. Through these a strong current of air is drawn by means of a fan, which also forces the furnace gases first through sheet-iron cooling pipes and then through a series of woollen bags, in which practically the whole of the fume is deposited as a fine blue powder. The arrangement of the bag and of the bag house is similar to that of the paint room for refined fume subsequently figured and described.

Along the front of each furnace is an iron apron or workplate, and the lead overflows from one corner of the hearth into a



Figs. 22-25.—The Jumbo, Double, or Moffet Hearth.

casting pot (not shown in the figures), set in a cylinder 31 inches diameter and 44 inches deep, and kept hot by a small fire of wood. The molten lead is drawn off by a pipe and stopcock into a row of moulds placed on a truck below, the pigs of lead weighing 84 lbs. each. The fuel is inferior bituminous coal, the consumption being 8 per cent. of the ore, and the quicklime used is about 2 per cent. of the ore. Each fire is worked by two men on each eight hours' shift, so that there are twelve

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smelters required for the whole furnace in twenty-four hours. The daily capacity depends chiefly upon the endurance of the men, and varies from 24 short tons (of 2000 lbs.) in summer to 30 short tons in winter. About 68 per cent. of the lead present is converted at once to metal, 22 per cent. going into the slag, and, owing to the hot blast, no less than 10 per cent. is converted into fume; the loss in condensing this fume by the bag process employed is practically *nil*.

The furnace is worked as follows*:—After throwing on a charge the fire remains undisturbed for one to one and a-half minutes, during which time lead is reduced and the mass becomes crusted over on top. One of the two smelters then plunges a pointed bar into the melted lead at one end of the fire, and using the edge of the trough as a fulcrum prises up the mass, raising up cakes of slag and letting down undecomposed ore and fuel. In this way, he works right to the other end of the fire, while the second man, following with a long-handled shovel, picks out the lumps of glowing fuming slag, which are first laid on the workplate to drain, and then tossed into a water box to cool. When the fire has been worked through by the first smelter with a pointed bar he takes the shovel, while the second man works through the fire again with a broad paddle. They then both use shovels to pick out as much slag as can be seen, after which they scatter over the fire a new charge, consisting of two shovelfuls of coal and five or six shovelfuls of ore previously mixed with about 2 per cent. of lime. The operation of working and charging takes about two minutes, and the interval of rest between each operation is about one and a-half minutes. During this interval the tools are left resting on the workplate with their handles in swing hooks, while the ore oxidises and is reduced to metal. As already mentioned, 68 per cent. of the lead present is obtained directly in pigs, and as the ores contain usually about 73 per cent., this amounts to about one-half the weight of ore treated. Most of the zinc in the mineral goes into the slag together with 22 per cent. of the lead.

It is obvious that the working of the Moffet hearth is cheaper than that of any other form of hearth, but unless it is intended to make pigment (which can only be successful under exceptional circumstances, the market being limited) the ordinary hearth is more advantageous, as it treats in proportion to its size almost as much ore, and yields a larger proportion of lead as pigs.

Comparison between Reverberatory and Hearth Methods.—The advantages of hearths over reverberatories are:—(1) Smaller consumption of fuel for given capacity; (2) less first cost and greater facility for repairs; and (3) convenience which they offer for interrupted work and short campaigns. Their disadvantages are:—(1) Necessity of machinery for pro-

* Dewey, *loc. cit.*, p. 682.

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ducing a blast; (2) larger amount of labour required and its comparatively skilled nature; (3) greater liability of the men to lead poisoning; and (4) much higher volatilisation losses. It will be obvious that the hearth process is most suitable in out-of-the-way places, where labour is cheap and fuel dear, especially if water power can be obtained for the blast, and where the supply of ores is irregular; it is only under very exceptional circumstances to be recommended in localities of cheap fuel, dear labour, and regular ore supply. Galenas rich in silver should never be treated by the hearth process, as the losses by volatilisation are so high; at Bleiberg (Carinthia) the average loss of lead was found to be 2 per cent. higher than in the Carinthian furnace.

Treatment of Bye-products.—The bye-products of the ore hearth differ in no marked degree from those of the reverberatory, they are two—viz., grey slag and fume. The former, like the reverberatory grey slag, always contains a large proportion of metallic lead mechanically intermixed with the mass of silicates, sulphates, and oxides forming the true slag. Both products are commonly smelted together in a hearth or low blast furnace provided with a firebrick lining, brasque bottom, and external iron crucible or kettle, and blown by means of one or two tuyeres at the back. The products are an impure lead, "slag lead," which is hard even after poling, a very dark "black slag," which is thrown away, and a good deal of fume, most of which is generally lost. The old English slag hearth is well described by Percy*; but as this appliance has been mostly replaced by more modern cupolas and blast furnaces similar to those employed in smelting low grade lead ores (*v.* Chap. viii.) it is unnecessary to enter into details here.

The Lewis and Bartlett Bag Process.

This process, which is in use at the Lone Elm Works of the Picher Sublimed Lead Company, and also at those of the Bristol Sublimed Lead Company, is peculiar in its aim to produce as much fume as possible; by the use of special fume filtering apparatus, and by taking special precautions in the smelting, more than one-half of the lead contained in the grey slag and flue dust from the ore hearths is worked up into a fine white pigment. The fine flue dust and fume "blue-powder" from the ore hearths, owing partly to the carbonaceous and bituminous matter and partly to the finely-divided metallic sulphides contained in them, burn readily when piled in heaps on the ground and ignited by means of oiled waste, and after a few hours' smouldering are converted into a mass of pinkish-white crusts. Analyses of raw and roasted "blue powder," as well as of flue

* *Metallurgy of Lead*, pp. 413-417.

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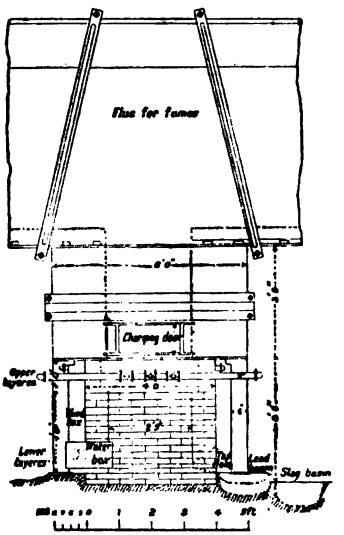
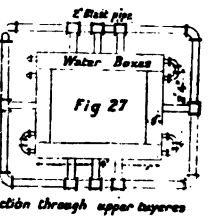
dust from the first dust chamber and of grey slag from the Moffet hearth, are given in Table XI. The grey slag contains 21·45 per cent. of metallic lead which stays on a 60-mesh sieve, and the remaining portion, according to the analysis given in the Table, contains 47·45 per cent. of lead in combination, making a total of 58·71 per cent. in all.

The modified slag hearth or "slag-eye furnace," in which the grey slags and blue powder are worked up together, is 2 feet square by 6 feet high altogether, the distance from lower tuyeres to the charging door being only 2 feet 3 inches, and the charging door 4 feet from the ground. Its construction will be understood by reference to Figs. 26 and 27.* Blast is supplied by means of eleven 1½ in. tuyeres passing through water-boxes; four of them are at the bottom for fusion and reduction, the remaining seven being only a few inches below the charging door in order to secure as much volatilisation as possible. The furnace is kept filled to the charging door with a bed of glowing coke, upon which the charges are spread. All the bye-products of the ore hearth are treated in this furnace together with a small amount of oxidised ore. An average daily charge for one furnace is made up as follows :—Grey slag, 2800 lbs.; "blue powder," 1000 lbs.; "dry bone" (oxidised lead and zinc ores), 600 lbs.; half refined blue powder from cooling pipes, 450 lbs.

The object being to volatilise lead rather than to reduce it,





Figs. 26 and 27.—Lewis and Bartlett Process—Slag Hearth.

the top of the furnace is run so as to keep the flue nearly red hot. It is found that a hot flue is necessary for the production of a good white colour in the pigment, and with the same object only hard Connelsville coal is used as fuel. The waste heat in the

* Dewey, *Trans. A.I.M.E.*, vol. xviii., pp. 683 and 689; lately this furnace has been improved by replacing its brick walls with water-jackets.

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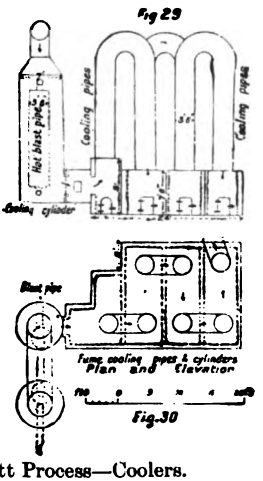
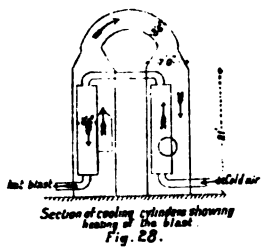
furnace gases is made use of in order to heat the blast, which also assists in volatilising lead. In spite of all endeavours a considerable proportion of lead is, however, reduced, and this, together with the poor "black" slag formed, finds its way through a hole in a "tap-plate" at the bottom into an iron "lead basin" with two unequal compartments, the larger being filled with charcoal. The slag flows over the charcoal into the "slag basin" placed below, through which a stream of water flows, while the lead filtering through the charcoal passes under the partition into the smaller compartment, whence it is ladled into moulds. This lead is of very inferior quality, and has to be remelted and poled to fit it for sale; about 13 pigs, or 1100 lbs., are produced on an average daily. The slag is nearly black, and, though still carrying a fair percentage of lead, is thrown away, except a small proportion which is thrown into the furnace against badly corroded places in the walls as a partial protection.* Dewey gives an analysis showing 23 per cent. of PbO in this slag, but it is reported to contain under 10 per cent. now.†

The furnace is started by lighting a fire on the bottom and filling the shaft with charcoal free from breeze, after which a light blast is started; when the charcoal is glowing, a thick bed of coke is charged and the full pressure of blast (9 ozs.) turned on. As soon as this is thoroughly ignited on top the ordinary charge is given, each charge consisting first of a bed of coke, distributed chiefly towards the front and centre of the





Figs. 28-30.—Lewis & Bartlett Process—Coolers.

shaft, then of slag which is heaped against the back and sides so as to protect them somewhat, and, lastly, the blue powder. Two men attend the furnace on each 8-hour shift, one to feed, and one to ladle lead and wheel slag.

A Baker blower (No. 5) supplies air through an 18-inch main

* *v.* Note on previous page as to use of water-jackets.
† *E. and M. J.*, Dec. 8, 1894.

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to three of these "slag-eye" furnaces, two of which are run together, the third being in reserve. From the flue a fan (6 feet diameter and 3 feet face), run at 290 revolutions per minute, draws the fumes and gases, first, through a pair of iron cylinders 7 feet diameter and 20 feet high, lined with firebrick, through which the 18-inch blast main, temporarily enlarged to 3 feet, passes in order to heat the blast, and, secondly, through a series of four inverted U pipes, $3\frac{1}{2}$ feet diameter and 20 feet high, set in brickwork and exposed to the air. These cooling arrangements are shown in plan and elevation in Figs. 28, 29, and 30. Some fume settles out in the pipes, but it is of poor colour and

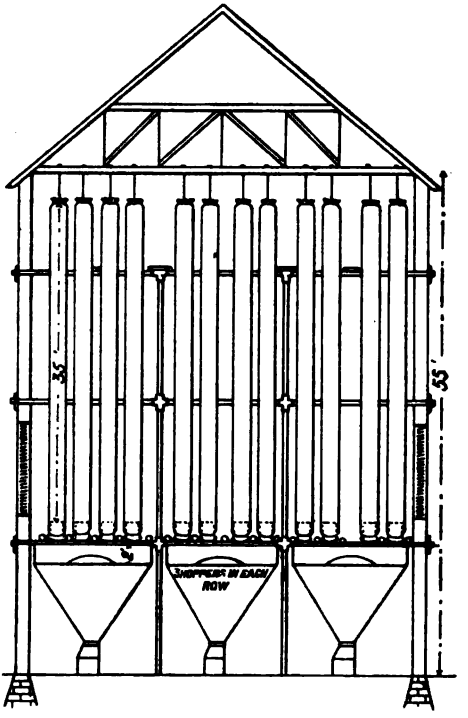

Fig. 31.—Lewis & Bartlett Process—Filter.

is therefore returned to the furnace. After passing through the cooling pipes the fumes enter the white bag room, or "paint house," which is 90 feet by 40 feet by 45 feet high in two storeys with a boarded floor, the arrangement of which may be seen from Fig. 31. There are three rows of hoppers, nine in each row, and above each hopper are suspended twenty bags of coarse flannel made from unscoured wool, 20 inches in diameter and 35

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feet long, costing $9 apiece, and tied over nipples projecting from the top of the hopper. The bags are suspended from the rafters, the hoppers and flues are also suspended by means of iron straps from a skeleton flooring of 1½-inch pipe laid 2 feet apart across a framework of 2½-inch pipe, which is itself supported by eighteen columns of 3½-inch pipe. Each bag has 168 square feet surface, so that the filtering surface of the whole 540 bags is 88,704 square feet.

The paint from different parts of the room is of about the same quality, and has good body and colour. It is packed in barrels holding 500 lbs. each, and sells at a slightly higher price per lb. than pig lead, 1 lb. of which makes 1·6 lbs. of paint. The daily product of each furnace is about 4250 lbs.

Analyses of the white paint as well as of the various intermediate products of the process are given in the following table:—

TABLE XI.*

	Grey Slag.	Chamber Dust.	Flue Dust.	Blue Powder.		White Paint.	Black Slag.
				Raw.	Roasted.		
SiO_2, . .	12·70	2·76	2·54	0·12	0·10	0·08	...
FeS_2, . .	0·67	...	...	...	...	...	...
ZnS, . . .	3·64	5·57	0·11	...	...	...	...
PbS, . . .	14·73	51·59	10·41	7·59	...	...	...
$PbSO_4$, . .	5·18	22·74	61·39	45·08	48·76	65·23	...
PbO, . .	33·55	3·79	11·47	44·55	46·82	25·87	...
ZnO, . .	14·53	0·35	0·42	0 42	0·27	5·98	...
MnO, . .	...	...	...	...	...	...	...
FeO, . . .	...	...	...	...	...	...	...
Fe_2O_3, . .	2·90	0·93	0 97	} 0·07 {	0·32	0·03	...
Al_2O_3, . .	0·78	0·06	0·05		0·05	...	...
CaO, . .	11·49	6·40	5·24	0·07	0·48	0·02	...
MgO, . .	0·12	0·03	0·03	...	...	...	...
CO_2, . . .	...	3·83	1·35	0·19	0·90	1·77	...
SO_2, . . .	...	0·86	...	0·55	1·65	0·02	...
HgO, . .	...	...	...	...	0·37	0·72	...
Org. matter yielding:—							
CO_2, .	...	14·41	7·38	1·93	...	...	..
H_2O, .	...	3·38	3·53	3·18	...	...	...
	...	...	...	...	99·72	99·72	...

* From Dewey, *loc. cit.*

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CHAPTER VI.

THE ROASTING OF LEAD ORES.

The Roast-Reduction Process.—The roast and reduction process is adapted to the treatment of ores with any kind of metallic and non-metallic admixture, siliceous ores, and those containing arsenic and antimony being always treated in this way. It comprises the separate operations of *roasting* and *smelting*.

In the *roasting* process as much as possible of the arsenic, antimony, and sulphur are driven off, and the lead is, as far as possible, converted into oxide. Some lead sulphate is unavoidably formed, but its amount is usually kept to the lowest attainable limit, since, in the ordinary reducing smelting, it would be reduced to sulphide. In many cases, towards the end of the operation, the temperature is raised in order that the silica may react upon the sulphate, forming silicate, and at the same time partially fusing the material so as better to fit it for smelting.

In the ordinary *smelting* process conducted in blast furnaces ("cupolas" or "stacks"), the lead is reduced from its oxide, partly by means of carbonic oxide, but chiefly by direct contact with masses of glowing, porous fuel (coke or charcoal). Such lead sulphide as may remain in the roasted ore or become reduced from the sulphate is also decomposed by the action of iron reduced from its oxide, the lead being liberated while the sulphur forms an *iron matte*. Other metallic constituents of the ore, except gold and silver, which are collected in the lead, pass either into the slag or the matte or become volatilised.

Ores may be roasted in lump form or as fines. All classes of ore were formerly roasted in lump form, but the method has been quite superseded as regards ores in which lead is the predominant constituent, and is now only employed for highly pyritic ores, which roast very well in large lumps.

Reactions of the Roasting Process.*—The commonest class of lead ore is a more or less finely pulverised mixture containing besides galena, varying proportions of blende, pyrites, chalcopyrite, quartz, and other gangue materials.

The reactions which take place in roasting such mixtures are as follows:—

The first action, as the temperature of the charge rises, is the distillation of about one-third of the sulphur in the pyrites, which

* *v.* Roberts-Austen, Pres. Address, Brit. Assoc. Meeting at Cardiff, 1891; also Rose, *Metallurgy of Gold*, in this series, pp. 216-220.

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TABLE XII.—ANALYSES OF COMPLEX LEAD SULPHIDE ORES.

	Przibram, Bohemia.	Rodna, Transylvania.	Goslar, Lower Harz.	Clausthal, Upper Harz.	Mechernich, Rhenish Prussia.	Col. Sellers, Leadville, Colorado.	Broken Hill, N.S.W.	Sunny Corner, N.S.W.
Reference,	1.	2.	3.	4.	5.	6.	7.	8.
PbS, . . .	45·09	54·57	10	74·09	69·74	18·67	28·90	16·30
ZnS, . . .	8·73	0·99	36	7·46	0·22	28·73	37·20	22·00
$CuFeS_2$, . .	0·12	tr.	1·5	1·15	0·51	tr.	tr.	4·50
FeS_2, . .	4·65	42·62	24	0·60	1·39	49·29	0·50	37·30
Sb_2S_3, . .	1·07	0·02	...	0·80	0·11	...	...	...
Ag_2S, . .	0·313	0·067	...	0·10	0·017	...	0·091	...
MnS, . .	...	...	...	...	...	2·61	...	...
SnO_2, . .	0·14	...	...	...	...	...	...	...
$FeCO_3$, . .	13·77	...	...	2·27	...	...	...	...
$MnCO_3$, . .	1·61	tr.	...	0·48	...	...	...	...
$CaCO_3$, . .	1·75	tr.	...	1·71	1·57	...	...	...
$MgCO_3$, . .	0·57	...	...	0·35	...	...	...	...
$BaSO_4$, . .	...	...	20	...	...	...	...	...
$CaSO_4$, . .	...	...	...	1·92	...	...	...	...
SiO_2, . . .	20·05	0·49	8·5	8·57	22·05	0·96	32·00*	16·50
Al_2O_3, . .	1·63	...	...	1·32	3·60	...	...	...
As, . . .	...	0·34	...	...	...	tr.	...	0·30
Ag. ozs. per ton,	89·3	19·3	...	28·5	34	7½	21	12

NOTES.—1, 4, 5 are mixtures of ore and concentrates; 6 and 7 are natural ores which have to be concentrated before roasting.

References.—1. *E. and M. J.*, July 16, 1892. 2. Hofman, *Metallurgy of Lead*, p. 167. 3. Schnabel, *Handbuch der Metallhüttenkunde*, vol. 1., p. 389. 4. *E. and M. J.*, Oct. 21, 1893. 5. Schnabel, *op. cit.*, p. 393. 6. Taylor and Brunton, *E. and M. J.*, May 8, 1886. 7 and 8. Author.

burns with a blue flame to SO_2, part of which again in contact with oxygen and with the hot porous charge and furnace brickwork is converted into SO_3. The next action is the successive oxidation of the metallic sulphides by the current of hot air, approximately in the following order, Fe_3S_4, $CuFeS_2$, Ag_2S, Cu_2S, PbS, ZnS. Of these, *silver* sulphide is soon reduced to metal, and would remain so if it occurred alone, but the presence of much base metal sulphides and excess of free SO_3 enables it to be converted into sulphate; *iron* and *copper* sulphides are converted, in the first instance, into sulphates, *lead* and *zinc* sulphides chiefly into oxides, free SO_3 in the vapours reconverting part of the oxides into sulphates.

* This is not silica, but a mixture of silicates, including rhodonite, garnet, felspar, &c., as well as quartz.

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This process of oxidation is not continuous, except in a strong draught, for as soon as the sulphurous acid reaches a certain tension chemical equilibrium is established and the oxidation is arrested, even in presence of an excess of oxygen, unless the temperature be raised considerably.

Besides a temperature which should be easily controlled, efficient oxidising roasting, therefore, requires abundant access of air to the hot ore and rapid removal of the products of combustion. If the temperature be kept moderately high, and the draught and supply of air low, most of the lead and zinc will be converted into sulphates, partly by direct action of SO_2 and O, partly by the SO_3 evolved from decomposing iron sulphates The temperature must, in any case, be well under control, for, if raised too suddenly, portions of the ore will undergo incipient fusion, and particles of unaltered sulphides be protected by an envelope impervious to the further action of the gases.

As the temperature rises, and before the oxidation of the sulphides is complete, the sulphates formed begin to dissociate in the following order—$Fe_2(SO_4)_3$ $FeSO_4$, $CuSO_4$, Ag_2SO_4, $ZnSO_4$. *Iron* and *copper* sulphates give off, at first, SO_3, and, afterwards, SO_2 and O; *silver* sulphate remains undecomposed until all the iron and nearly all the copper sulphates have been decomposed, when it in turn breaks up into metallic silver, oxygen, and SO_3; *zinc* sulphate is nearly unchanged in simple roasting, giving off only part of its SO_3 at a full red heat, the basic sulphate remaining not being decomposable under a bright yellow heat. *Lead* sulphate is unaltered.

Among gangue substances *quartz* and *barytes* remain unaltered, *chalybite* is converted into magnetic oxide, and *calcite* into calcium sulphate.

As regards removal of the deleterious substances, *arsenic* and *antimony*, it may be remarked that *mispickel* (FeSAs) is pretty thoroughly decomposed, the greater part of its arsenic being volatilised direct as As_2S_3, which is oxidised into As_2O_3 and SO_2 by the current of hot gases, the remainder being oxidised direct to As_2O_3 at a low temperature in presence of a good draught.

Most *sulph-antimonides* and *sulph-arsenides* (*e.g.*, fahlerz, bournonite, &c.), like mispickel, give up the greater part of their arsenic (antimony) as $As_2S_3(Sb_2S_3)$, which are at once oxidised to $As_2O_3(Sb_2O_3)$ and SO_2. Another portion of the arsenic (or antimony) is converted into arseniates (or antimoniates), which resist the effects of simple heating. These compounds are, however, reduced in contact with metallic sulphides, especially with free pyrites, and, therefore, on rabbling the arseniate (or antimoniate) formed in the oxidised surface crust gets turned over into the bottom layer of the ore, where there is more or less free sulphur, and is re-volatilised to the surface as

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$As_2S_3(Sb_2S_3)$, so that it gets another chance of escape. *Enargite*, however, is only partially decomposed, most of the arsenic remaining behind as arseniate. It is noteworthy that, whereas the ferric arseniate produced in small quantity by the oxidation of mispickel is comparatively easily decomposed by means of heat and reducing agents (carbon or sulphur), *cupric arseniate* formed by partial oxidation of enargite is most obstinate in resisting decomposition; in fact, according to Pearse,* scarcely any of the arsenic of enargite can be driven off by roasting, even when assisted by the subsequent rabbling in of fine coal.

Simple *arsenides* and *antimonides* (*e.g.*, smaltite, domeykite, dyscrasite) are much more difficult to decompose, by far the larger part of their arsenic remaining as stable arseniates and antimoniates of the metals present (iron, copper, and silver). Such minerals, therefore, like the *sulph-arsenides*, should, whenever possible, be roasted together with an excess of sulphides, such as pyrites; use is also made of this reaction of sulphur upon combined arsenic in the treatment of arsenical furnace products.

That a large part of the antimony, as well as arsenic, which is expelled from antimonial and arsenical ores during roasting escapes as sulphide is proved by the fact, noted by Wendt,† that in kiln roasting lump ore, crystals of artificial *stibnite*, as well as of *orpiment*, were found in the flues and on the upper and cooler portions of the charge. The occurrence of *orpiment* and *realgar* on the upper surface of roast heaps is a matter of every day observation.

Sinter and Slag Roasting.—When at the end of the roasting proper the temperature is suddenly raised so as to agglomerate or fuse the charge, the lead sulphate formed during roasting is decomposed by means of silica (either already present in the ore or added, if necessary, in the form of more siliceous ores); for, although lead sulphate is practically unaltered at the temperature reached in the furnace, free silica drives out the sulphuric acid in accordance with the equation—

$$PbSO_4 + SiO_2 = PbO \,.\, SiO_2 + SO_3.$$

Even when the temperature does not rise high enough to decompose lead sulphate, there is more or less combination between silica and lead oxide, so that the mass begins to soften and agglomerate without actual fusion. At the temperature of fusion *calcium* and *barium* sulphates in the roasted ore are also partially converted into silicates, as well as *iron oxides* to a greater or less extent, according to the perfection of the fusion. *Zinc* is to a small extent volatilised, but is mostly melted down, with the oxides of iron and lead, into a very fusible double silicate.

* *Trans. A.I.M.E.*, vol. xviii., p. 62. † *Ibid.*, vol. xix., p. 100.

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The final result of the combined roasting and melting process is a fluid or pasty mixture of oxides and silicates never quite free from sulphides, which is tapped out into iron moulds, and, after being broken up, forms a material better suited to blast furnace treatment than the fine powder resulting from plain roasting.

The difference in the condition of a blast furnace resulting from the use of slagged or sintered sulphide ores, instead of the plain roasted fines, is remarkable. Much greater regularity in working is accompanied by much more rapid smelting, and by a smaller coke consumption, while the losses in slags and flue dust are much diminished, and the percentage of sulphur being much less, the amount of matte produced is smaller. In view of these advantages, "slagging" or fusion would be universally adopted in place of simple roasting (in spite of its greater cost both for fuel and labour), but for the heavy volatilisation losses involved. According to Newhouse,* the average loss in plain roasting silver-bearing lead ores containing 12 to 18 per cent. lead is from 2 to 5 per cent. of the lead and hardly any of the silver, while in fusing down the same ore the loss is increased to 15 or 20 per cent. of the lead and 2 to 3 per cent. of the silver. The lead loss in simple roasting at a low temperature is chiefly as fine dust mechanically carried off by the draught and recoverable in suitable flues and settling chambers, while the loss in the fusion process is as a true fume, very little of which is recovered in ordinary flues. The losses in slightly "sintering" or "agglomerating" are not very much higher than in plain roasting, therefore rich lead ores should be only "sintered," never "slagged." With ores rich in lead the agglomeration need not be carried very far, a very slight rise in temperature above that normally employed giving the material sufficient plasticity to enable the furnacemen, by dint of ramming it into the slag pots as drawn, to produce coherent masses, which only partially break up before charging, and are, therefore, much less liable to furnace losses than mere powder. According to Hofman,† only such ores should be slagged as contain under 10 per cent. of lead and 100 ozs. of silver per ton. The general feeling among metallurgists at present is to fix the limit of silver for fusion very much lower, say at about 30 or 40 ozs., and of late years the method has dropped very much out of use.

As a general rule, it may be said that as much ore as possible should be plain roasted, only sufficient being sintered to keep the furnace open. The different modes of roasting should be employed as follows:—

Plain (*and slightly agglomerating*) *roasting*, for all simple

* *E. and M. J.*, Feb. 28, 1891.

† Discussion on "American Improvements, &c.," *Trans. A.I.M.E.*, vol. xxii., p. 657.

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galenas, as well as for all mixed ores, when rich either in lead or in silver, or both.

Sinter- and slag-roasting, for pyritic, arsenical, antimonial, and blendiferous ores poor both in lead and silver; pyrites and mispickel concentrates carrying gold, &c., quartzose gold ores when obtainable forming a convenient flux.

When the ores to be fused contain less than 10 or 15 per cent. lead, the charges have to be roughly calculated, so as to contain silica and iron in suitable proportions to form a fusible slag. This is readily done, as almost every large smelting works treating custom ores will have both pyritic and quartzose ores at command. Lime is rarely added to a charge in the fusion hearth, as sufficiently good slags can always be made with iron alone and whatever lead or zinc may be present.

As to the *rapidity* of roasting, the richer the ore in lead the slower must be the roast, and the lower the temperature at the fire end of the furnace throughout the entire operation.

Roasting Appliances.—Examples of all the following are in use at different localities for the roasting of lead ores—viz., heaps, stalls, kilns, reverberatory furnaces, and shaft and muffle furnaces.

ROASTING OF LUMP ORES.

Heap roasting is only applicable to lump ores. Fines may be employed in certain proportions as a covering, but if it is wished to use them in large proportion they must be "bricked" or "balled" with an admixture of lime or of waste liquors containing ferrous sulphate. A single roasting in heaps is usually not sufficient, and, as a rule, several roastings are required.

In the heap roasting of mixed ores there is always a tendency for the copper (and, according to Vogt, for cobalt and nickel also) to become concentrated in a "kernel," which resembles in composition a copper matte of 7 to 50 per cent.* According to Plattner,† when the roasting proceeds very slowly silver and lead exhibit a well marked tendency to pass towards the *outside* of the lump; for example, in a well roasted piece of heap-roasted iron-lead matte the central kernel contained only 5·2 per cent. Pb and 0·075 per cent. Ag, whereas the outer envelope contained 17·2 per cent. Pb and 0·230 per cent. Ag. This is confirmed by the fact that films of metallic silver have been not infrequently found on the outside of lumps of calcined ore, where, no doubt, they had been deposited by the decomposition of some volatile compound of the metal. When, however, the roasting proceeds quickly, so that the temperature rises to the fusing point of a low grade matte, copper, lead, and silver are all concentrated

* *v.* Peters, *Modern Copper Smelting*, 7th Ed., 1895, p. 134; also Schnabel, *Handb. der Metallhüttenkunde*, vol. i., p. 36.

† *Die Metallurgischen Röstprozesse*, Freiberg, 1856, p. 205.

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indiscriminately by a sort of liquation process into a low grade matte which is found in the lower portions of the pile.

At *Goslar* (Lower Harz) heap roasting is still practised on the pyritic ores from the Rammelsberg, which carry blende and barytes, but are too poor in lead and silver for the more costly roasting in reverberatories. The ore is composed roughly as follows:—

	Per cent.
Galena,	9 to 10
Blende,	27½ to 30
Chalcopyrite,	1 to 1¾
Pyrites,	11 to 16
Gangue (chiefly barytes),	44 to 47

Average composition.

	Per cent.
S,	16 to 18
Ag,	0·011 to 0·015
Cu.	0·45 to 0·55
Pb,	9·98 to 10·5
Zn,	18 to 19
Fe,	5 to 7

The floor of the roast yard is formed of well tamped clay, upon which is spread a layer of roasted fines. The heaps hold 300 to 500 tons each, and are built up on a square bed of logs and brushwood 16 to 20 inches thick and 33 to 40 feet in the side, channels being left for the air currents. Upon this bed is spread, first, the coarsest ore, which comprises the chief part of the heap; then, successively, the pieces of fist, egg and nut size; and, lastly, a layer of raw fines. The heap is then covered with a layer of sifted once-roasted fines, and forms a truncated pyramid on a square base 36 to 40 feet square at bottom and, say, 12 feet square at top. When ready, it is lit on the side opposite to the wind. In this way, since the air can only enter through the channels left in the bed of fuel, during its passage through the lower part of the heap it becomes deprived of its oxygen, so that the hot gases which reach the upper part of the heap are composed principally of nitrogen and sulphurous acid. These gases volatilise from the pyrites a part of its sulphur, which condenses in a liquid form in bowl-shaped depressions about 8 inches across formed in the upper part of the heap and lined with ore fines, from which it is from time to time removed. The first sulphur appears fourteen days after lighting the heap.

The first roasting lasts from six to seven months, after which the coarse ore is screened from the fines (which are leached for zinc vitriol * and then smelted) and subjected to a second and even a third similar roasting conducted under sheds to protect it from the weather and from high winds. The second roasting lasts six to eight weeks, the third from four to six weeks. The coarse well roasted ore is then smelted † together with the leached fines.

The roasting of 100 tons of ore requires altogether 13·9 cubic metres (3·8 cords) of billet wood and 212 faggots of brushwood. It will be readily understood that in the foregoing complicated

* *v.* Chap. xiv. † *v.* Chap. xi.

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series of operations there is great danger of losing lead and silver in fine ore dust mechanically carried away by the wind, &c., especially as, in the roasting process, silver appears to become concentrated in the outermost thoroughly calcined shell of each lump of ore, where it is most liable to loss by abrasion, &c.—the exact opposite being the case with copper.

At *Sunny Corner* (N. S. Wales) a complex ore, composed chiefly of pyrites, quartz, and blende, with 6 to 10 per cent. of galena and 3 to 4 per cent. of chalcopyrite, is roasted in heaps of from 800 to 2000 tons. No care is taken to separate the fines from the coarse ore by screening, but an even bed of wood is loosely laid in chequer work about 15 to 18 inches high, and upon this is piled, first, a layer of large lumps of ore, and, afterwards, the "run of mine" ore as trammed direct from underground. The heap is built from a tram line about the level of its top by means of iron-turning plates and movable sections of track as described by Peters. Every few yards upright logs of wood are inserted into the roast bed, which, soon igniting and burning away, form chimneys for ensuring a good ventilation in the pile. The quantity of wood used for each ton of ore is very slight, and its cost but a few pence per ton, as, with this very pyritic ore, wood is only required for ignition purposes, and the ore once ignited burns readily and thoroughly. A heap of ore can be thoroughly burnt out in about two to three months if left alone, but by commencing to remove the burnt ore as soon as the outer fringe is properly roasted, the whole heap can be burnt out and removed in a month when not over 7 or 8 feet high.

Stall Roasting.—Roasting in stalls is very similar to heap roasting, except that on account of the steadier draught the process goes on somewhat quicker; and that a portion of the fumes is frequently drawn off through the back wall of the stall and discharged into the air through a high chimney. A very convenient form of stall for this purpose is that figured below, and commonly used in many places for roasting copper as well as lead ores.

The *Wellner* stalls used at Freiberg have a sloping bottom, and require no "roast bed" of wood. They can be used either with or without chimney draught, and are built in pairs, sloping up towards a common centre. Each of the four short sides of the double stall contains four small arched fireplaces, starting from each of which is an arched channel built of large lumps of ore selected out as the stall is being filled; through these the products of combustion and the roast-gases can find their way to the central portion of the stall and thence upwards. When the stall is filled, these fireplaces are kept going only until the outer edge of the layer of ore is thoroughly ignited, after which no further fuel is required. If part of the ore has to be re-

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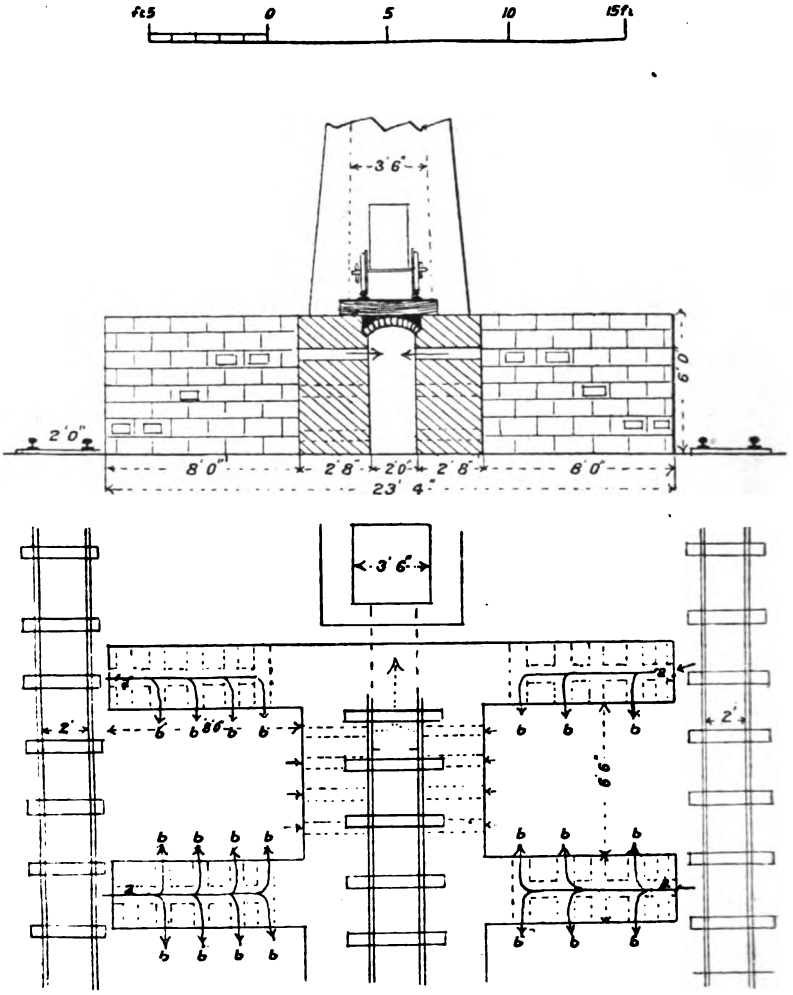
roasted, only one side of the double stall is filled and lit, the other being reserved for the re-roasting. The length of each half stall is 8 to 10 feet, and the width 10 to 12 feet across the four fireplaces.



Figs. 32 and 33.—"Wellner" Stall for Roasting.

The only advantage of stalls of this kind is that any kind of cheap inferior fuel can be used in them; they are, however, awkward and expensive to fill and empty, especially when wood

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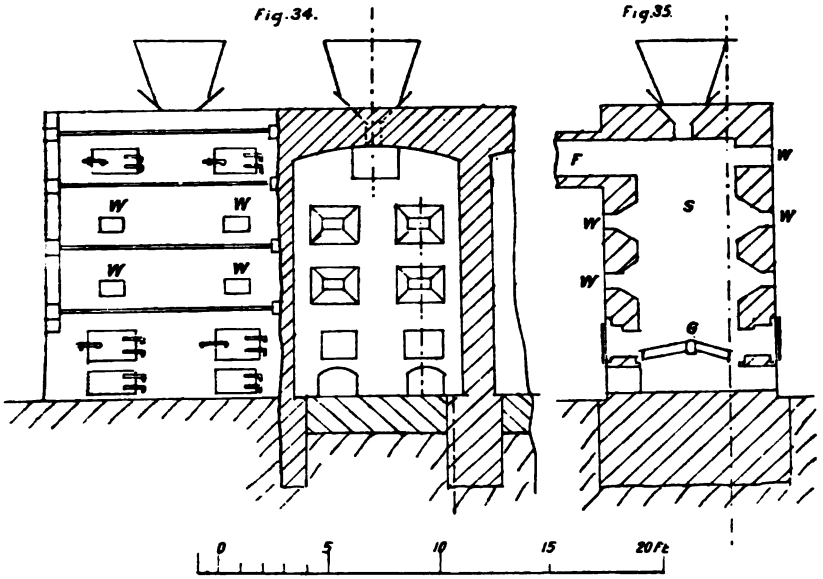
of any kind is very scarce; they are only in use for lead ores at a few out-of-the-way places. The form of stall here figured, however, is of very wide application, one of its special advantages being the air passage, *a*, in each of the division walls communicating with the open air, by which means the ore in each stall is virtually exposed to the air (through the openings, *b*, *b*) on both sides as well as on the front, and not on the front only as in the old pattern of stall.

Kiln Roasting.—Kiln roasting is only employed when the roast gases produced from pyritous lead ores can be usefully made into sulphuric acid, or when they *must* be rendered innocuous to the surrounding country. The ores treated must



Figs. 34 and 35.—Freiberg Kiln.

be poor in lead, or it is impossible to prevent them from sintering.

Kiln roasting requires no fuel, as, once started, the necessary heat is supplied by combustion of the sulphur; skilled labour is, however, indispensable, and the roasting with leady ores is so imperfect that it must be followed by a re-roasting of the lump ore in heaps, and of the smalls in reverberatory furnaces. Ordinary pyrites burners are unsuitable for ores containing much galena, as the column of ore is too low to give the requisite temperature.

Lead ores containing much pyrites are successfully roasted in

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kilns at Oker (Harz) and at Freiberg. The construction of those at the latter place is shown in Figs. 34 and 35. S is the shaft of the kiln, 9½ feet high, 7½ feet long, and 4 feet 3 inches wide. It is filled with ore through an opening in the arch by means of a hopper closed by a sliding door, or, better, by means of a cone and bell. The ore falls upon the pierced saddle grate, G, and is ignited through the ashpit doors, A, through which also the supply of air is regulated. The roast-gases are led off through a flue, F, in the back wall into a main flue, which is common to the whole system of kilns, and communicates with the sulphuric acid works. The roasted ore is raked out through the discharging doors, D, and the descent of the column is regulated by means of the working doors, W, through which bars can be driven into the charge to loosen it and break up half-fused masses. Each kiln turns out 1½ tons of roasted ore per twenty-four hours.

At Oker similar kilns, arranged in groups of five, communicating with each other under the arch, are used for roasting mixed copper and lead ores. The kilns are somewhat higher than those at Freiberg, being 13 feet high by 7 feet 6 inches long and 4 feet wide, and the charge per division varies from 1·4 up to 2 tons per twenty-four hours. Clean pyritous copper ores are so well roasted in these kilns as to leave barely enough sulphur to form matte with the copper; but the leady or mixed ores averaging blende 25 per cent., pyrites 25 per cent., chalcopyrites 15 per cent., galena 14 per cent., heavy spar 11 per cent., and other gangue 7 per cent., and of which 1·8 to 2 tons are charged per twenty-four hours, cannot be sufficiently desulphurised at one roasting. They are, therefore, re-roasted twice in heaps to fit them for smelting.

Comparison between Different Systems of Roasting Lump Ore.—The following table shows at a glance the advantages and disadvantages possessed by heaps, stalls, and kilns respectively:—

	Heaps.	Stalls.	Kilns.
Cost of erection and repairs, .	*Nil*,	Medium,	High,
Cost of working labour, . .	About equal in quantity.		
,, ,, fuel, . .	High,	Medium,	Almost *nil*.
Perfection of roast with ordinary leady ores, . . .	Poor,	Better than heaps,	Worse than heaps.
Utilisation of roast gases, .	*Nil*,	Partial.	Almost complete.
Danger of loss of silver by dusting and leaching, . .	Greatest,	Intermediate,	Least.

It is, of course, understood that only the coarser parts of ores which are rich in pyrites can be at all advantageously roasted in lump form. Such ores, however, which are usually roasted in heaps, can frequently be handled to greater advantage in stalls or kilns. In many cases the value of the sulphuric acid

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produced by condensation of the roast-gases added to the amount of compensation for damage to crops, &c., saved by preventing the escape of the fumes will more than pay interest and wear and tear on a complete plant of kilns and acid chambers; again, in other cases, the arsenic contained in the ore will pay a good interest on the cost of kilns and settling flues, even if the whole of the sulphurous and sulphuric acids in the roast gases be allowed to escape, while in cases where none of these bye-products can be advantageously utilised or rendered marketable, and when the surrounding country is barren, simple heap-roasting is often the cheapest and best system, even when it has to be repeated on part of the ore.

ROASTING OF FINE ORES.

The greater part of the lead ore received by any smelting establishment is in a more or less fine condition, whether in the form of natural smalls from the mines or, as is more common, of concentrates from dressing works, which may vary from bean size jig concentrates down to the finest dust from revolving tables and other slime machines. The variety of appliances which have been used for roasting fine ores is very great; they may be described as reverberatory, cylinder, muffle, and shaft furnaces, examples of all of which will be described in the volume of this series on the *Metallurgy of Copper*.

The roasting of lead ores presents, however, much more difficulty than that of copper ores, since they are so much more fusible, while it is often complicated by the presence of large amounts of blende, one of the most difficult of all metallic sulphides to thoroughly oxidise. Some of the roasting furnaces which have been most successful on pyritic copper ores have proved quite unsuitable to the roasting of ordinary galena ores carrying blende, while other forms of furnace are so obviously unsuitable that they have not been even tried.

The furnace which has been most uniformly successful in roasting lead ores is the old-fashioned long hearth reverberatory, which, though not economical of fuel or of labour, is adapted to ores carrying any proportions of galena or of pyrites.

In all cases the reverberatory hearth is connected with a system of flues and condensing chambers in order to catch the particles of ore mechanically carried over by the draught, together with some lead volatilised in the metallic condition through the reaction of PbO and $PbSO_4$ on PbS in the hottest part of the furnace, and a still larger amount of PbS* there volatilised.

* Lead sulphide being far more volatile than the metal itself, its oxide or sulphate.

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REVERBERATORY FURNACES.

The old style of reverberatory furnace with a single hearth, on which the charge was spread evenly for roasting and from which it was raked at the end of the operation, is now almost extinct (except, perhaps, in Wales), as it is not only of small capacity, but is extremely wasteful of fuel.

Double Hearth Reverberatories having the hearths superposed ("double bedded calciners") are still to be found at Mechernich and one or two other works in Germany and in England, but have been generally abandoned elsewhere on account of the heavy labour required to work the charge on the upper hearth by means of movable platforms on which the men stand, and of the difficulty of getting at the lower hearth and arch for effecting repairs when necessary. The saving in fuel effected by the superposition of hearths, though real enough, is, in most cases, insufficient to compensate for the above disadvantages. Beyond this and a slight saving in first cost, the chief advantage of the "double bedded calciner" is the economy of space in old metallurgical works where there is not room to erect new furnaces of the long type.

The superposed hearths of the Mechernich furnaces are very long, being each 50 feet long by 13 feet wide. In twenty-four hours, each furnace puts through 9 tons of lead ore dressed up to 50 to 60 per cent. lead, with a consumption of 27 cwts. of coal (*i.e.*, 15 per cent. by weight of the ore), the roasted ore, which is sintered together before being drawn, averaging only 0·6 to 0·7 per cent. of sulphur. No such perfect roasting of lead ore is conducted in America, but it takes a good deal of labour, and would be, in most cases, far too expensive under American conditions.

Other double hearth reverberatories are in use for roasting silver ores, and will be referred to in Part II.

Single Long Hearth Reverberatories.—The commonest kind of roasting furnace is the German "Fortschaufelungsofen" or long hearth reverberatory, containing at the same time several charges in different stages of the process, which are successively raked and pushed forward as the completed charges are drawn.

When the subsequent treatment of the roasted ore requires it to be in a fused or agglomerated condition, the roasting hearth at the firebox end terminates, either in a "sump" or depression in which the semi-fused mass can be collected, or, preferably, in a vertical channel or flue through which the roasted ore is raked into a separate smelting hearth or fuse box, and through which the flames passing over the latter ascend to the roasting hearth. When a separate fusebox is used, the ore is almost always made so fluid as to be drawn off through a spout into slag pots, and only if very infusible is it raked out in agglomerated cakes and

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masses through the working doors. In America, when agglomeration of the ore is desired, this separate smelting hearth is almost invariably, while in Europe, on the other hand, the continuous hearth with sump is usually, employed.

The disadvantage of the latter is that the heat cannot be so well concentrated, and the mass begins to soften and sinter together as far back as the third or fourth door from the fire-bridge, which not only increases the difficulty of rabbling, but, unless the hearth is exceedingly long, results in an imperfect roast, particles of unaltered sulphides becoming glazed over, and so protected from oxidising influences. On the other hand, the volatilisation losses both of lead and of the precious metals are much less in the sump reverberatory than in the separate fusion hearth. The arguments for and against "sintering" and "slagging" respectively have been already stated in this chapter, and need not be repeated here. Suffice it to say that the rich non-ferruginous ores commonly treated in Europe are best roasted in the sump form of reverberatory, while the ferruginous concentrates and ores which are more usually met with in America are best treated in that with separate fusion hearth.

General Considerations.—The length of the hearth from flue to firebridge, or to the beginning of the smelting hearth, as the case may be, varies from about 40 feet, in the case of galena ores comparatively free from pyrites, up to 60 or 70 feet, in the case of ores containing much pyrites, half of the sulphur in which is available as fuel. Reverberatory hearths have been constructed of much greater length than these, but it may be safely stated that no increase above the maximum length of about 70 feet is warranted, for any further trifling economy of fuel is more than offset by the increased labour required to handle the charges, the increased cost of construction resulting in no compensating advantage. The width of the hearth should be as great as possible, consistent with reasonable facility in handling the ore. It may be as little as 9 feet 6 inches and as much as 17 feet, but the capacity of the narrow hearths is much smaller in proportion to their cost, and modern furnaces are generally from 14 to 16 feet wide. Beyond 17 feet nothing would be gained by increasing the width, for, in the first place, the handling of the charge would be more difficult, and, in the second place, arches of much more than that span at the very low rise of $\frac{1}{2}$ to $\frac{3}{4}$ inch to the foot generally adopted would not be very safe under the alternate expansion and contraction caused by changes of temperature.

It is of great importance to make the arch as flat as possible, so that the flames may be well spread out towards the sides, instead of travelling along in the central channel of the roof, and doing comparatively little work upon the ore. For the more complete utilisation of the heat contained in the products

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of combustion before their escape from the furnace, the arch is sometimes built with a slight downward inclination toward the flue. The same effect, however, is much more readily produced by inclining the hearth upwards in the same direction, either by giving it a uniform gentle slope or in steps, the latter plan being preferred by some on account of marking off conveniently the area occupied by each of the separate charges.

The arch is best constructed of firebrick throughout,* though it is quite usual to employ selected red brick in the part furthest from the fire. The actual hearth is always constructed of the best firebrick obtainable, so as to better resist the wear and tear of the tools. At the far end of the furnace the bricks are laid on edge (and sometimes even on the side, though this is really poor economy), but near the firebridge they are best laid on end, and, of course, the sump or fusion hearth must be so laid.

The number of working doors is made as small as possible, so as to reduce both the first cost and the subsequent cooling of the furnace; but if they are placed too far apart the difficulty of handling the charges is much increased. In practice the distance varies between 6 and 8 feet, the most common distance being from 7 feet to 7 feet 3 inches from centre to centre of the cast-iron door frames. The blocks of masonry between adjacent working doors are in modern furnaces kept as small as possible. The skew backs of the arch must be supported between the door frames, either by means of special plates cast with a strengthening rib; of wrought iron I girders inserted behind the buck staves; or, finally, of a sheet of boiler plate, say 18 inches wide by 1 inch thick. The buck staves are almost invariably of old rails, which are more convenient to obtain than I beams, though the latter are considerably stronger for equal weight.

An essential condition of quick and economical roasting, often lost sight of, is the provision of a supply of heated air in close proximity to the surface of the ore. Merely passing an excess of air through the fireboxes, besides being wasteful of fuel, is not nearly so effective as furnishing a separate supply of fresh air previously heated by passage through the hollow division walls of the firebox, through the bridge, or even through hollow flue walls, and under the hearth.

The quantity of ore put through in twenty-four hours depends on the percentage of sulphur expelled; on the prevailing mineral accompanying the galena, whether pyrites, quartz, or blende, the first being the quickest and the last the slowest to roast; on the efficiency of the workmen; and on the final condition of the roasted product, whether pulverulent, sintered, or fused. The capacity of furnaces of the same area may vary in accordance with the above factors between 6 and 14 tons per day,

* Unless they cost over three times the price of common brick.

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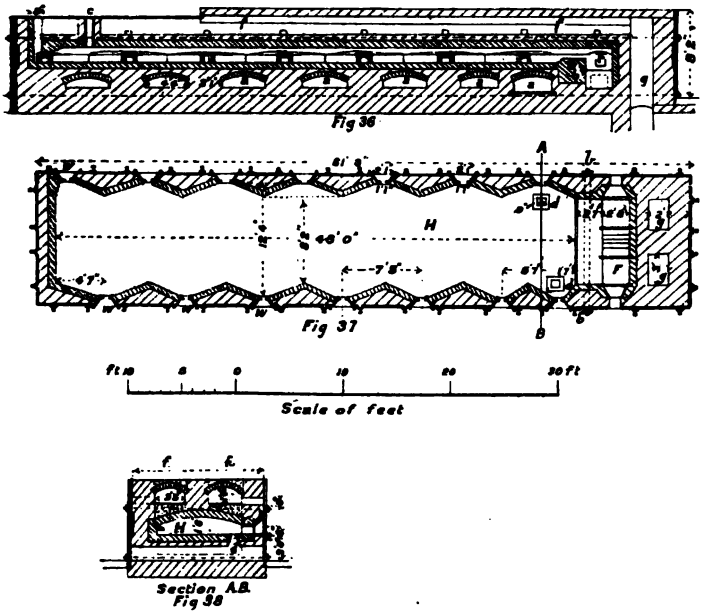
the average lying between 8 and 12 tons. The consumption of fuel is greater than with pyritic copper ores; if coal be used it varies between 15 and 30 per cent. of the weight of ore put through, averaging 20 to 25 per cent., according to the quality. If wood be used, the consumption may vary between two and four cords per day, as it may be reckoned that two cords of wood will be a little more than equal to 1 ton of coal. The amount of labour required varies also with the composition of the ore and the condition of the roasted product, but, as a rule, three men are required to a shift, which may be either of eight



Figs. 36-38.—Reverberatory Furnaces—Przibram.

or of twelve hours, generally the former in America and Australia, the latter in Europe. If the roasted ore is turned out in a powdery condition, a capacity of 2 tons per man may be regarded as a reasonable maximum; if it is to be slagged, the capacity is rarely, if ever, over $1\frac{1}{3}$ tons per man, and may fall below 1 ton per man.

Examples of Reverberatory Furnaces.—As an example of the long hearth reverberatory arranged for plain roasting without sintering that in use at *Przibram* may be quoted, and is shown in Figs. 36, 37, and 38.* In these F represents

* From Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 334.

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the fireplace fired at both ends; *b*, the bridge, built of magnesia brick and cooled by a long cast-iron water-box; H is the hearth, 48 feet long and 10 feet 3 inches in average width, or equal to 12 feet 4 inches as usually measured. It will be noticed that the fourteen working doors, W, are not placed in pairs opposite each other as in the Freiberg and most American furnaces, but alternating; this arrangement much facilitates the even working of the charge, and is widely adopted in the most modern roasters. The ore is let down through the charging pipe, C, at the flue end of the hearth in charges of 1 ton each and spread out through the two doors at that end, being gradually worked forward towards the bridge, and finally, when roasted, raked through the discharging doors, *d*, into a small truck running in the first arch, *a*, which is provided with a floor of cast-iron plates. Similar arches run across the furnace at intervals, their function being merely to cool the hearth. The furnace gases rise through the vertical flue, *e*, and turn back under a floor of cast-iron plates which serves for drying the ore, after which they follow two brick flues, *f*, built over the firebrick arch and fire grate, finally turning down beyond the latter through the flues, *g*, which are provided with dampers and connected with a main underground flue.

The ore roasted in this furnace contains 51 to 58 per cent. galena and 8 to 11 per cent. blende, with 12 to 14 per cent. silica, the remainder being chiefly iron pyrites and chalybite. It is roasted down to an average of only 1 per cent. S, and is very slightly agglomerated with the rabbles at the end of the operation before dropping into the hot-ore truck.

The Freiberg furnace for sinter roasting is shown in Figs. 39 to 41. It is somewhat similar to that just described, but the portion of the hearth marked S is the sump, sloping gradually to a trough between the first working doors, through which the agglomerated ore is raked into iron wheelbarrows.

With very rich lead ores the melting point is so low that perfect *fusion* of the charge can be easily effected in a sump furnace without separate fusebox. This was done at *Mine La Motte* (Mo.)* in the case of a rich galena concentrate poor in silver. The hearths vary in length from 55 to 66 feet and in width from 11½ to 13 feet, the length being generally five times the width, with ten doors on each side, and a continuous slope of 18 to 20 inches. The grate is made 3 feet 6 inches deep from bridge to grate bars so as to use wood fuel. The bridge and firebox division wall are air cooled, a small chimney on the roof above the latter drawing a strong current of air through both ends of the hollow bridge and keeping it cool. As in the Freiberg furnace, the "sump" in which the ore is fused down is com-

* Hofman, *Metallurgy of Lead*, 1893, p. 166.

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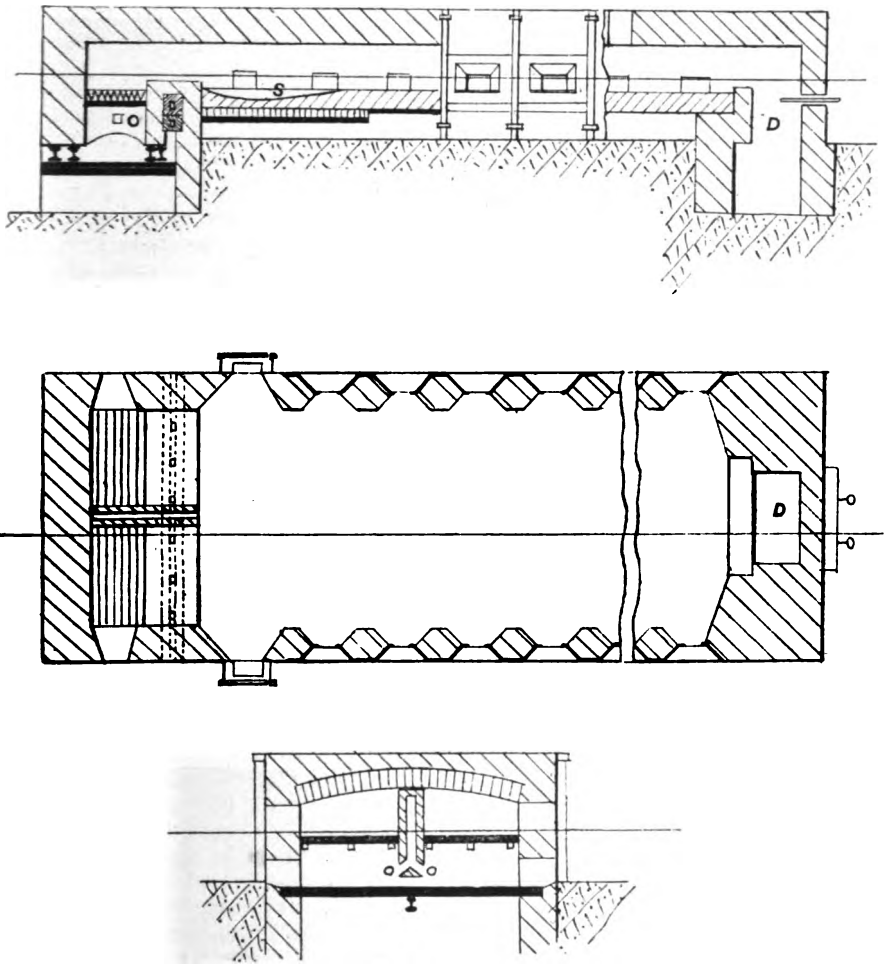
posed of a single course of firebrick built into a wrought-iron pan resting on brick pillars, between which air circulates freely; this air cooling is very effective in preventing corrosion.



Figs. 39-41.—Freiberg Furnace or Sinter Roasting.

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The dressed galena contains 65 to 75 per cent. Pb, and the "sulphides" (a sort of middle product of galena and pyrites) 15 to 30 per cent. Pb, 16 to 45 per cent. Fe, and 1 to 5 per cent. Ni and Co. The roasting charges are made up of a mixture of both products, 8 tons per day being treated in the 55 by 11½ feet furnaces, and 10 tons in the 65 by 13 feet furnace. The roasting is carried on in the following way :—*

As soon as one fused charge is drawn, sand is thrown over the sintering hearth near the bridge and the fire lowered while the next charge (already desulphurised down to 5 or 6 per cent. sulphur) is spread over it, and each successive charge moved forward two doors, a fresh charge being dropped in at the flue end of the furnace and spread. This operation of moving forward and adding a new charge takes about two hours. The doors are now closed and the fires cleaned and fed; the proper amount of sand is thrown upon the charge to be fused and well rabbled in. The fire is then urged for four hours, the fuse charge being well stirred every hour. When ready for drawing, the men, protected by a half-cylinder of boiler plate, which stands on the ground below and in front of the working door, rabble out the fused mass (which is described as of a "ropy" consistency) with long hoes direct through the working doors and subsequently break it up by throwing water on it, when it cracks and is easily shovelled into wheelbarrows. Sometimes a little lead is reduced in the furnace by "reactions," but this trickles away through a small hole in the bridge into the ashpit, whence it is recovered by washing the ashes. Eight tons of ore are roasted and slagged per twenty-four hours. Other data are given in Table XIII.

The "Colorado" roaster, with separate "fusebox" or smelting hearth, is shown in Figs. 42 to 46. The particular furnace figured is from the *El Paso Smelting Works;* it is peculiar in that the furnace gases are turned under the hearth through vaults occupying the whole width, which thus become dust chambers. The arrangement is a poor one as the cleaning out of dust chambers in such a situation is a particularly hot and dusty job, and more or less interferes with all the work of the roaster shed while it is going on; it is only defensible where there is no room for proper dust chambers. Vaults under the hearth are never required, and the space is much better filled with rabble masonry or simply with well-tamped sand, as the temperature of the calcining hearth rarely gets above a dull red, except very near the bridge. The fusion hearth must, of course, be built on a vault.

The furnace figured has four hearths, each 14 feet square, separated by means of 3-inch steps, the end farthest from the fire being thus closest to the roof so as better to utilise the heat of the roast gases. The same result might be attained by dis-

* Kemp, *S. of M. Quarterly*, vol. x., No. 3, p. 215.

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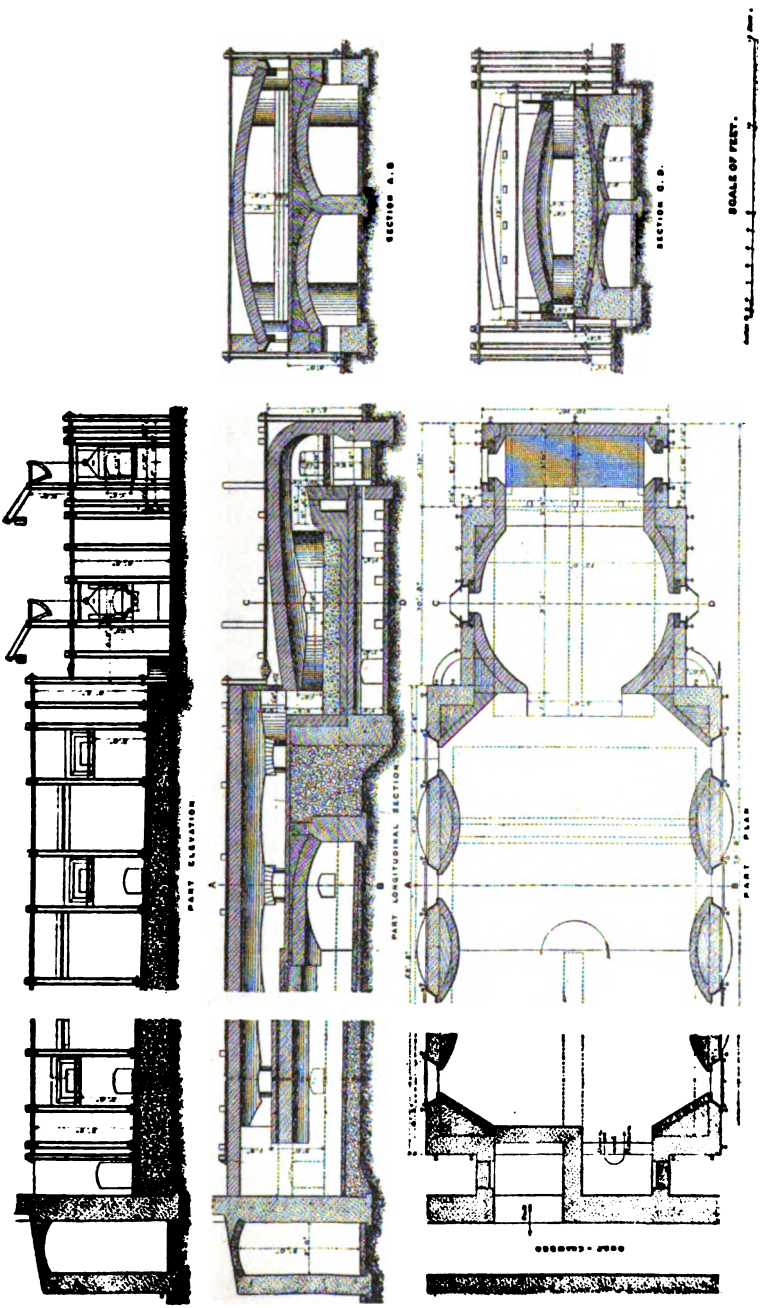

Figs. 42-46.—The Colorado Roaster.

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pensing with the drops and giving the hearth a continuous gentle downward slope towards the bridge.

The fusion hearth is nearly circular in plan, the radius being 10 feet 8 inches; connection is made with it from the smelting hearth by means of a vertical flue 26 inches high and 5 feet 6 inches long by 16 inches wide, the object being to ensure a sharp separation between the smelting temperature below and a roasting heat above where the hot gases suddenly spread out from 5 feet 6 inches to the full width of 14 feet. In this way the ore above is to a considerable extent prevented from fritting together until the moment of its arrival on the fusion hearth, a result favourable to the handling of the charge as well as to the perfection of the roast, and impossible to obtain with the Freiberg form of furnace, where, with fusible ores, the charge sometimes begins to agglomerate as far back as the third or fourth pair of doors.

The arch of the furnace is generally built of firebrick only up as far as the end of the lowest roasting hearth, the rest being picked red brick, but some metallurgists prefer to build the whole arch of firebrick, as being more lasting and avoiding the evils caused by unequal expansion and contraction. The bottom of the roasting hearth is formed of firebrick set edgewise as closely as possible on a bed of red brick; while the working bottom of the fusebox, formerly built up (as shown in figures) of quartz sand melted down with a small quantity of slag on a concave brick bottom, is now commonly made of a simple inverted arch of firebrick properly wedged up, which is found to be very durable and satisfactory. The whole of the fusion hearth is enclosed in heavy cast-iron plates, and a heavy plate is also inserted in the air-cooled firebridge to take the longitudinal stress off the hearth. The walls of the smelting hearth and the flue leading to it from the roasting hearth wear rapidly and have to be patched with fireclay from time to time. The cost of a furnace like that figured is, at Denver, about £600, on the Mexican frontier about £1000. Each furnace requires 86,000 red bricks, 15,000 firebricks, 10,000 lbs. of old rails, 12,000 lbs. of cast iron, and 4400 lbs. of wrought iron (sheet iron and tie-rods).

The weight of charge is from 2400 to 3300 lbs.; it is dropped through a hopper at the far end of the furnace and spread evenly over the space between the last four working doors, remaining there till a charge is again drawn from the fusebox, and the other charges have been moved forward a step, when it is all turned over and transferred to the second hearth. Besides the moving forward, each charge receives from one to three rakings with the rabble in the intervals so as to expose new surfaces. When it reaches the end of the roasting hearth, and before it is dropped on to the fusion hearth, the latter is prepared by spreading on it a few cwts. of siliceous ore to protect

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the bottom and to form slag with the ferruginous roasted ore. Frequently, also, flue dust is prepared for subsequent furnace treatment by being charged into the fusion hearth, where it is soon melted down after being covered with the hot roasted ore. As soon as the roasted charge has been spread the fire is urged as much as possible; fusion soon commences near the top, but frequent and vigorous rabblings at short intervals are required to lift up the siliceous ore and bring it into intimate contact with the more basic material and slag already formed. After a few hours hot firing the whole mass becomes fluid, when it is rabbled out into ordinary slag pots and left to cool; after which, it is broken up into lumps the size of a cocoanut for the blast furnace. When the charge runs high in lead the portions first fused must be rabbled out at once, as otherwise they would act too much upon the hearth and walls.

Furnaces like that above described will roast and slag from 6 to 10 tons per day with a consumption of 30 to 45 per cent. of coal, and leave from 2 to 6 per cent. sulphur in the product. When plain roasting, two men are found sufficient on a 12-hour shift, but when the charge is fused a third man is required to attend to the fuse box and the firing. With labour at 9s. 6d. to 10s. 6d. for twelve hours' work, and coal at 7s. 6d. per ton, the cost of roasting and fusing ordinary ores should not exceed 8s. per ton—though with unskilled men and slipshod superintendence it is frequently much higher.

At most Colorado smelting works of the present day the "fuse box" has been done away with, and in its place is often seen a separate "sintering hearth" the full width of the furnace, but at a lower level. This makes a sharp line between ore which is still roasting and that which is being agglomerated prior to drawing. In most cases the sintered ore is drawn into wheel-barrows or iron trucks, where it only partially coheres. At the *Globe*, and perhaps some other works, however, it is rammed into slag pots by the furnacemen and forms masses nearly as coherent and porous as coke, and, therefore, in the best possible condition for further treatment.

Other Examples of Long Reverberatories.—At the *Cockle Creek* works of the Sulphide Corporation, Limited, zinc-lead concentrates (middlings), and slimes containing 28 to 30 per cent. Pb and 25 to 28 per cent. Zn, are successfully roasted in long hand reverberatories, 62½ feet by 12 feet, for leaching by the Ashcroft process (*v.* Chap. xiv.). A moderately high temperature with low draught is employed, and the roasted product contains about 8 to 10 per cent. SO_3, besides some 3 per cent. of sulphur as unoxidised sulphide. Some further particulars are given in Table XIII. This table contains similar particulars with reference to all the furnaces described, and to a great many others as well.

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Reverberatories with Inclined Beds. — Reverberatory furnaces have been frequently built with a bed inclined at 1 in 3, or thereabouts, with the idea that in this way the hand rabbling, which is so costly, could be dispensed with, the weight of each fresh charge forcing the partially roasted ores down the slope. Furnaces of this description have been used successfully for years in Victoria for roasting auriferous concentrates, and the *Ferrari* * furnace of similar type is doing excellent work in calcining calamine ores in Sardinia, but it is probable that the tendency of leady ores to agglomerate would prove an insuperable objection to this attempt at a simple automatic furnace.

Mechanical Furnaces on the Reverberatory Principle.— Under this head might be considered the cylinder furnaces of various kinds, but the term "mechanical reverberatories" is usually restricted to those furnaces with a fixed bed in which the ore is rabbled or moved along by stirrers actuated by suitable machinery. Of this class are the O'Hara, the Brown-Allen and Brown Horse-shoe, the Pearce Turret, the Spence, Keller, Wethey, and Ropp furnaces.

The *Brown-Allen-O'Hara furnace*,† largely used in the Western States of America for roasting copper ores and mattes, consists normally of two superposed reverberatory hearths 90 feet long by 8 feet wide in the clear. The ore is moved forward by a series of stirrer carriages, which run on an iron track separated from the roasting hearth by means of a slotted wall, and which are attached to each other by chains running over a system of vertical pulleys at each end of the hearth. The ore fed in automatically at one end of the upper hearth is gradually moved forward by the stirrers till it reaches the far end, when it drops through on to the lower hearth. The stirrers run on in the air supported by the chains for a certain distance in order to cool them, and being turned over by the pulleys they then return on the lower hearth and gradually work back the ore to the discharging doors at the feed end of the furnace. The fireboxes, 3 or 4 in number, are built outside of the main furnace walls, the flames entering by cross arches.

The capacity varies from 20 tons per day when roasting down to 1 or 2 per cent. sulphur up to 35 tons per day when turning out calcines with 6 per cent. S. The cost of roasting in one of these furnaces at Denver is about 7s. 3d. per ton. The cost of a furnace is about £2000, ready for work; the chief drawbacks are the high fuel consumption and the frequent stoppages for troublesome and expensive repairs. These furnaces are in use at the *Globe Works*, Denver (Colo.), but the management is

* Mazzetti, *Rivista del Servizio Minerario nel* 1885.

† For figures and details *v.* Peters, *Modern Copper Smelting*, 7th Ed., p. 202; also Schnabel, *op. cit.*, p. 75.

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TABLE XIII.—Reverberatory Roasting Furnaces.

	Pribram, Bohemia.	Pennsylvania Smelting Works, Sandy, Utah.	Block 14 Smelting Works, Port Adelaide, S.A.	Cockle Creek Works, Newcastle, N.S.W.	Freiberg, Saxony.	La Motte, Missouri.	Mechernich, Rhenish Prussia.	Colorado Smelter, Pueblo, Colo.	Grant Works, Denver, Colorado.
Reference,	1.	2.	3.	4.	5.	6.	7.	8.	9.
Type of furnace,	A	A	A	A	B	B	D	A	C
Kind of roasting performed,	Plain	Plain	Plain	Plain	Sinter	Slag	Sinter	Sinter	Slag
Length of hearth (feet),	48′ 0″	78′ 0″	40′ 0″	62′ 6″	43′ 0″	55′ 0″	49′ 2″	65′ 0″	60′ 0″
Breadth of ,, ,,	10′ 3″	16′ 0″	17′ 0″	12′ 0″	10′ 8″	11′ 6″	13′ 1″	15′ 0″	15′ 0″
Area of ,, (in square feet),	496	1218	680	750	459	632	1286	975	900
Weight of each charge (lbs.),	2205	3000	2760	2205	3307	4000	...	3600	...
Number of charges per twenty-four hours,	4	6	9	10	8	4	...	8	...
Total output lbs. per twenty-four hours,	8820	18,000	24,840	22,050	26,460	16,000	19,845	28,800	22,000
Quantity in furnace at once (lbs.),	15,435	18,000	8280	11,025	16,535	32,000	...	36,000	...
Number of lbs. per square foot of area,	31	15	12	29	36	51	...	37	...
Time to roast each charge,	42	24	8	12	15	48	...	30	...
Percentage of lead in raw charge,	35-40	20	35-50	25-30	20-30	50-65	50-60	...	14
,, sulphur in raw charge,	12	30-40	20	14	20	16-29	12-15	25-30	25
,, ,, in roasted charge,	0·9	3-4	8-10	6-7	3-4	4-7	0·6-0·7	4-5	8
Description of fuel used,	Lignite	Coal	Coal	Coal	Coal	Wood	Coal	Coal	Coal
Percentage consumption of ditto,	35-38	...	18-20	20	25	62	15	24	27
Cost of fuel used per ton,	...	9/5	14/	4/	7/	...	...	6/3	...
,, roasting (labour),	...	...	5/	5/3	5/4	...	...	4/4	5/9
,, ,, (fuel),	...	...	2/10	/10	1/8	...	...	1/7	2/
Tools, repairs, and depreciation,	...	...	20/6	?	1/	...	...	?	1/6
Total cost per ton of ore,	...	6/ +	8/4	6/ +	8/	...	...	5/11 +	9/3

Types of furnaces.—**A** is plain reverberatory; **B**, reverberatory with sump; **C**, reverberatory with separate fusebox; **D**, double superposed hearth reverberatory having sump at end of lower hearth.

References.—1 and 5. Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 335. 2 and 9. *Private communications*, 1896. 6. Kemp, *S. of M. Q.*, vol. x., p. 215. 3 and 4. *Private notes*, 1897. 7 and 8. *Ibid.*, 1888 and 1897.

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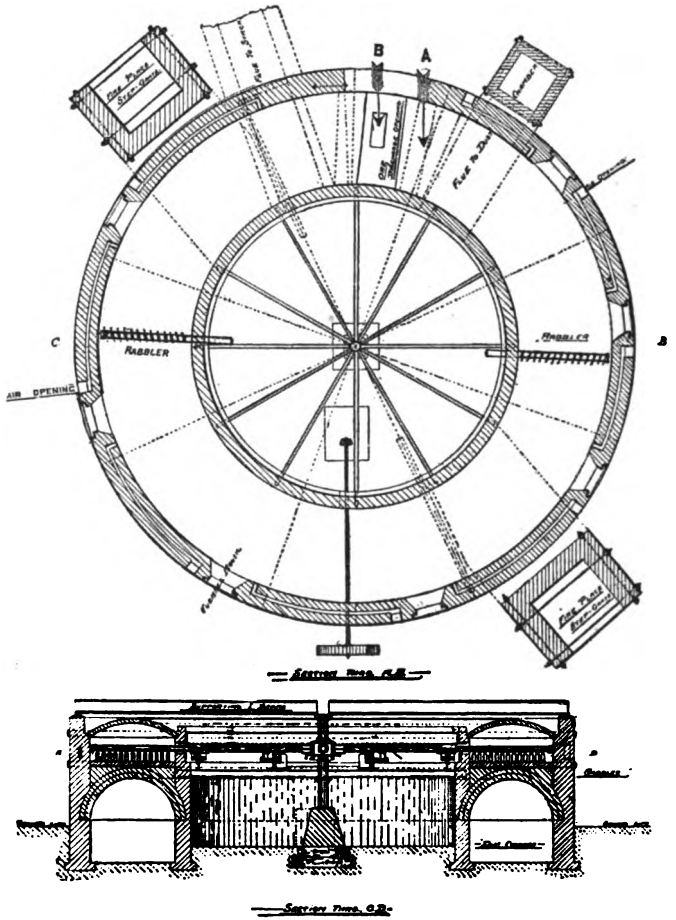
exceedingly reticent and no details are obtainable as to their performance.

The *Brown horse-shoe furnace* * may be considered as a Brown-Allen furnace with the upper hearth removed and the lower hearth bent round into four-fifths of a circle. Although doing



Figs. 47 and 48.—The "Pearce" Turret Roasting Furnace.

good work on zinc blende and copper matte, the author is not aware that it has ever been applied to lead ores. It will be described in Chapter x.

* *E. and M. J.*, May 12, 1894; also Peters, *op. cit.*, 1895, p. 218.

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The *Pearce "Turret" furnace*,* invented by Mr. R. Pearce of the Argo Works for roasting pyritous ores, concentrates, and copper mattes, has been used for roasting leady ores and mattes with good results. The general construction of this furnace is shown in Figs. 47 and 48, from which it is seen to be a reverberatory hearth built in a circular form with an open space inside the circle. In the centre of this a vertical column supports four horizontal radiating arms of 5-inch pipe, to which are attached rabble blades for stirring the ore, and which can be revolved at any desired speed. The pipes are perforated inside each of the ploughs or rabbles, and air forced through the pipes escapes through the perforations, cooling the arms and rabbles, while at the same time supplying a current of hot air to promote oxidation and accelerate the roasting. To allow of a continuous slot in the inner wall of the circular hearth through which the arms must pass, all that side of the arch is supported by stirrups from eight 12-inch I beams arranged radially over the top of the furnace. The crushed ore is fed at A by means of a hopper, is pushed along the circle at any desired speed by the rabbles, and discharged automatically at B into iron tramwagons underneath. The hearth is heated by two stepgrate fireplaces automatically fed with coal, and the whole space underneath the hearth is utilised as dust chambers. The rabble blades have to be renewed every three or four weeks, beyond which the cost for repairs is very trifling. The cost of a 36-foot furnace in Denver is about £1000, so that it is considerably cheaper than any other mechanical furnace in first cost. One man only per shift is required to clean the grates and attend to the furnace.

This furnace in Colorado is roasting mattes containing 10 to 12 per cent. lead, 30 to 35 per cent. copper, and 21 per cent. sulphur down to 6 per cent. S at the rate of 13 tons per day and at a total inclusive cost which is stated to be under 3s. 6d. per ton, including power, repairs, and depreciation. At the *Selby* Works (Cal.) it roasts lead mattes containing 8 to 12 per cent. lead down to 4 per cent. sulphur at the rate of 14 tons per twenty-four hours.† On ordinary pyritous ores containing some silica and no lead the capacity is somewhat greater, and the total inclusive cost on such ores in Colorado is only 3s. per ton.

Both at the *Colorado* and *Philadelphia* Smelting Works (Pueblo, Colo.) furnaces of this pattern have been erected. At the former works, however, they have been discarded owing to the slow roasting on leady material, high fuel consumption, and large amount of flue dust produced. At the latter works the furnaces are still in use, but give much trouble and are disliked on this account by the management, although the actual roasting is done cheaper than in the hand furnaces—viz., for a trifle under

* For details consult Peters, *op. cit.*, 1895, pp. 215, *et seq.*

† Douglas, *Journ. Soc. Arts*, Aug. 16, 1895, p. 832.

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4s. per ton. On very leady ores it has been found convenient to use only one of the rabble arms instead of two (or four as at first proposed by the inventor). The ore takes five hours to pass through the furnace, the daily output being 15 tons; one man attends to two furnaces on each shift, but the coal consumption is nearly twice as much as with hand furnaces and the

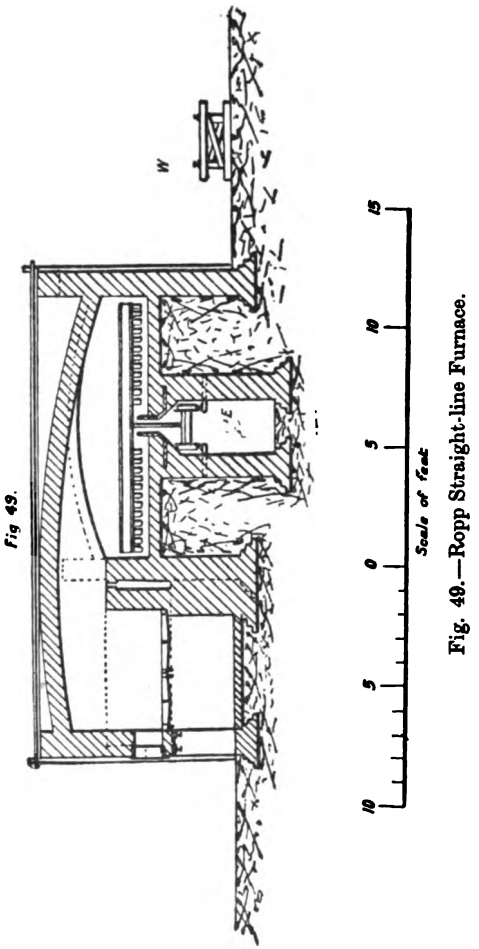

Fig. 49.—Ropp Straight-line Furnace.

amount of flue dust produced is from 3 to 4 per cent. as against one-half per cent. or less for the hand furnaces. Sintering on the hearth is combated by a heavy adjustable plough for tearing

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up the crusts—the invention of Rhodes.* It is a significant fact that none of the lead smelters who have had experience

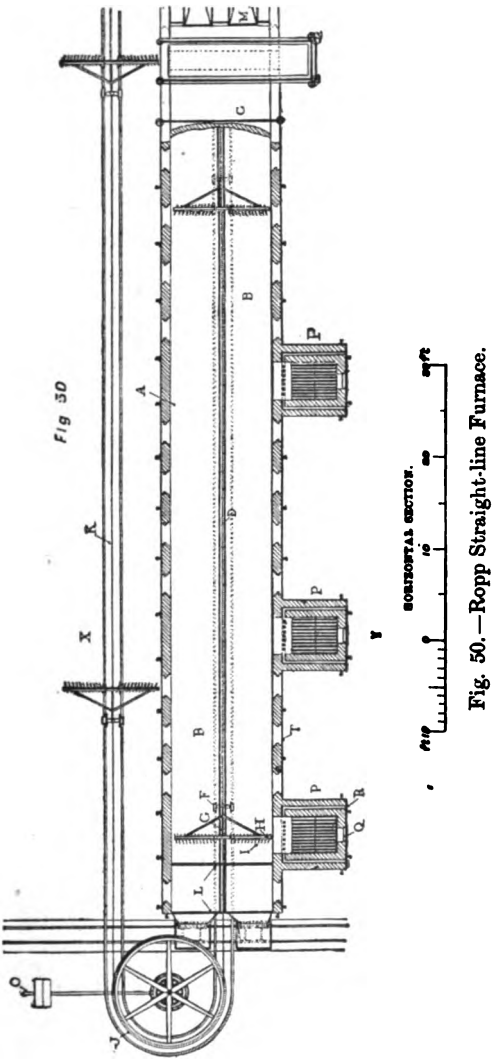

Fig. 50.—Ropp Straight-line Furnace.

with the Turret furnace are at all pleased with it for their work.

* Supt. Philadelphia Smelting Works.

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The *Ropp straight-line furnace* * has proved one of the most successful of all mechanical furnaces on leady material. Some of the details of the furnace will be understood from reference to Figs. 49 and 50. The rabble blades are supported on carriages which, instead of running on a track level with the hearth, and only separated from it by means of a sheet-iron curtain (as in the Brown-Allen O'Hara furnace), run in a vault beneath the arch, connection being made by vertical arms which pass through a continuous cast-iron slot in the centre of the hearth. These arms are attached to a wire rope instead of to a chain, and while both rope and carriages are much better protected from the heat of the hearth than in the O'Hara furnace, they are more than half their time outside the hearth altogether, so that they get thoroughly cooled down at each revolution, which takes three and a half minutes. The ropes pass round two large sheaves at the furnace ends, and the track for the stirrer carriages bends round outside the furnace, as shown in the figures, so that the carriages run continuously with the rope without any jerking or irregularity of motion. The length of hearth in the ordinary or small-sized furnace is 105 feet by 11 feet wide in the clear, with four stirrer carriages and usually three fireplaces, arranged as shown in the figure. The ore is fed in from hoppers at one end of the furnace by means of Challenge automatic feeders, and discharged into roasted ore hoppers at the other end. There is no complication of superposed hearths, and the stability of the principal arch is in no way interfered with by openings; the furnace, therefore, suffers less from racking and wear and tear than most others, while it is easily accessible for repairs. The usual consumption of coal is 4 short tons per twenty-four hours, and 4 H.P. is required for moving the rabbles. Each furnace contains 66,000 lbs. of ironwork (costing £1150 f.o.b. San Francisco), 54,000 red bricks, and 23,000 firebricks. With red brick at 37s. 6d. per 1000, and firebrick at £5s 5s., the total cost of one furnace ready for work should not exceed £1800.

Some data of the performance of the furnace at the Selby Smelting Works (Cal.), compared with the work done by the Pearce Turret furnace—both furnaces running side by side at Selby on the same ore—are given in Table XIV.

On these figures there would seem to be some saving in cost in favour of the "Straight-line," but evidently its principal advantages are simpler construction and better cooling of the rabble blades (which means less cost for repairs) and the smaller amount of flue dust produced. It is no doubt the use of a blast for cooling the rabbles which increases the amount of flue dust produced by the Turret furnace. As regards economy of fuel, neither furnace seems to reach a high standard, and no doubt any of the more complicated furnaces with superposed hearths

* *E. and M. J.*, July 12, 1895; also *Private communications.*

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TABLE XIV.*—Comparison between Pearce Turret and Ropp Straight-line Furnace.

	Pearce Turret.	Ropp Straight-line.
Percentage of lead in ore,	12 to 15 per cent.	
,, of sulphur in raw ore,	20 to 25 ,,	
,, sulphur in roasted ore,	5 per cent.	4 to 5 per cent.
Dimensions of furnace,	36 feet diameter.	105 feet by 11 feet.
Approximate cost of furnace,	£1200	£1800
Time spent in furnace by each particle of ore,	Five hours.	Six hours.
Output of roasted ore per twenty-four hours,	12 to 16 short tons.	25 to 35 short tons.
Mean consumption of coal,	2 short tons.	4 short tons.
Percentage ,, ,,	15 per cent.	13 per cent.
Labour per furnace—day,	Two men.	Two men.
H.P. required to drive,	4 H.P.	5 to 6 H.P.
Repairs and depreciation, Flue dust produced,	Considerable.	Very little.

would give better results in this respect if they could always be depended upon to handle leady ores without clotting.

Some much larger furnaces of the Ropp type (150 feet by 14 feet) have been erected lately at the Port Pirie Works of the Broken Hill Proprietary Company for roasting rich galena concentrates from the dressing works at Broken Hill. Considerable difficulty is reported to have been experienced in roasting material so rich in lead owing to the clotting and incipient sintering which takes place, but detailed results are not yet obtainable.

At the *Hanauer* Works (Salt Lake City) a large Ropp furnace 180 by 16 feet is used for roasting all kinds of leady ore mixtures and is very much liked. The average charge contains 25 to 30 per cent. S, which is roasted down to 5 per cent. at the average rate of 35 tons per day, with a consumption of 5 tons (or 14·3 per cent.) of best nut coal. The amount of repairs is very slight, chiefly consisting in renewing the rabbles on the firebox side about once in six months, those on the opposite side lasting a year or more. To obviate trouble from sintering it is found advisable to use rabbles on the firebox side an inch shorter than those on the opposite side.

Mechanical Reverberatories with Multiple Hearths.—The best-known furnaces of this class are the *Spence* † and

* *Private communication* from A. V. I. Ropp, Nov., 1896.
† *v.* Peters, *op. cit.*, 1895, p. 220.

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Keller * furnaces. Both have superposed hearths (four in the Spence, five in the Keller) traversed by rakes having a reciprocating motion; but in the latter the mechanism and stirrer carriages are altogether outside the furnace, only the rabble-arm itself entering the hearth by means of a slotted wall. These furnaces are doing splendid work at Butte on pyritic copper ores and concentrates, but have not, so far as the author is aware, come into use for leady ores, trials at the *Germania* Works having proved unsatisfactory.

The *Wethey* furnace † may be regarded as a four-hearth furnace on the O'Hara principle. It consists of four superposed hearths, each 50 feet long by 10 feet wide, heated by a firebox at the side, and the ore is worked forward from the top hearth to the bottom by the usual stirrers of rabble blades fixed to pipes resting on carriages, which run on tracks fixed outside the furnace. The peculiarity which distinguishes this from the *Keller* furnace is that the rabbles, instead of having a reciprocating motion and returning upon their tracks, turn completely over and return upon the hearth immediately below, so completing the circuit and carrying the ore on each hearth continuously in one direction. The furnace is therefore virtually a four-hearth O'Hara.

A furnace of this type at the *Butte Reduction Works*, working on zincy and coppery pyritic ores, treats 30 to 35 tons per twenty-four hours, bringing down the percentage of sulphur from 40 to 6 or 8 per cent.; it consumes only 2 cwts. of slack coal to the ton, or 10 per cent. The cost for fuel and labour is only 1s. 6d. per ton, and the repairs in two years have been nominal in amount.

Of course, the results on lead ores would not be nearly so good as the above, yet it should be possible to work them; in fact, the author is informed that a furnace of this type is actually at work in an English works roasting galena concentrates from Broken Hill, but no details as to performance are available.

Revolving Bed Furnaces with Fixed Ploughs.—Examples of this type are the *Brunton*,‡ which, though the earliest of all mechanical furnaces (patented 1828), is still in use for roasting arsenical ores, and the *Bunker Hill* § rotary pan furnace, a very poor device, combining the disadvantages of hand and mechanical furnaces. Neither of these, however, is used for roasting lead ores.

The best furnace on this principle appears to be that of Blake,‖

* Douglas, *Journ. Soc. Arts*, Aug. 16, 1895; and Peters, *op. cit.*, pp. 214 to 218.
† *Private communication*, A. B. Wethey, Aug., 1896.
‡ Foster, *Ore and Stone Mining*, p. 614.
§ Rose, *Metallurgy of Gold*, p. 228.
‖ *Trans. A.I.M.E.*, vol. xxi., p. 943.

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which is on the principle of the Brunton, but instead of being supported on a central axis it runs on cast-iron balls in an annular groove 12 feet in diameter. It differs radically from the Brunton in two respects:—1. In having on its surfaces a series of concentric terraces, one above the other, so that each particle of ore pushed off one terrace by the fixed plough has actually to *fall* through the air on to the next terrace, instead of being merely pushed sideways still enveloped in sulphurous vapours. 2. In delivering upon the charge an independent stream of hot air unmixed with reducing gases. The heating of this air is effected by a pair of Siemens' chambers built in the usual way of brick chequer work, and heated, not by the waste gases, but by a separate fire, as the heat of the former was considered by the inventor to be insufficient. The air arrives upon the hearth in a nearly red hot condition, and thus very little fuel is required in the fireboxes. Its quantity being capable of accurate regulation the temperature of the hearth is *perfectly* under control—so much so that in treating a mixture of blende, galena, and pyrites the latter can be, if required, completely oxidised at a dull red heat without tarnishing the blende or fusing the galena.

The ease with which the temperature and rate of oxidation can be regulated with this furnace would seem to render success quite probable even on rich galena ores where only plain roasting without agglomeration is desired.

Revolving Cylinder Furnaces.—There are two main types of cylinder furnace, namely, the *Brückner*,* in which charging and discharging are intermittent, a single charge being put in and rotated until finished; and the *Oxland* † and *White* ‡ cylinders, in which charging and discharging are automatic and continuous, the inclination of the axis and speed of rotation combining to deliver the roasted ore at a constant though adjustable rate. Both types are often referred to as American inventions, but they are both of English origin, the *Brückner* cylinder being nothing more or less than Mactear's modification of Elliott and Russell's revolving black ash barrel, while the *White* furnace is practically identical with the *Oxland and Hocking calciner*, patented and erected in England several years before the first American "invention" of a revolving furnace. Both the continuous and intermittent cylinders are described and illustrated in Part ii., Chap ix. of this work.

Although giving very good results with argentiferous copper ores and mattes the *continuous cylinders* have not been tried on leady material, owing to the temperature not being sufficiently under control. Their capacity, however, is great; thus at *Briton Ferry* (Cape Copper Company) *Oxland* calciners, 60 feet long and

* Rose, *Metallurgy of Gold*, p. 229; also part ii., figs. 209 and 210.
† Foster, *op. cit.*, p. 615. ‡ Rose, *op. cit.*, p. 235.

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5 feet 6 inches inside diameter, roast daily 9 tons of white metal *dead* or 18 tons of coarse metal down to 10 per cent. sulphur.

Brückner Cylinders.—Many attempts have been made to apply these to the roasting of lead ores. At the *Germania* works (Utah) Brückner cylinders, 22 feet long by 8½ feet in diameter, gear-driven, are used for roasting both ore and matte, and put through 8½ tons each per twenty-four hours of pyritiferous ores containing 20 per cent. lead, roasting down to 2½ or 3 per cent. sulphur, while ores with 30 per cent. lead roast down to 5 per cent. sulphur in the same time; the fuel consumption in each case being about 20 per cent. of coal by weight. Even ores containing as high as 35 per cent. lead can be successfully roasted by adopting special precautions to keep the temperature low, especially at the neck of the cylinder and at the beginning of the roast. The marked success of the Brückner cylinders at these works, compared with results obtained elsewhere, is due partly to the unusually large diameter of the cylinders themselves, partly to greater care in regulating the firing, and partly to the adoption of special devices for equalising the temperature inside the cylinder, which the author is not at liberty to publish. By means of these precautions and devices sintering, or "balling," of the charge is of exceedingly rare occurrence, and even when it does occur accidentally the form of the cylinder permits of ready access for "barring off," &c. The revolving cylinder, however, has the disadvantage of making a very large proportion of flue dust and of being rather heavy in repairs, while, unless in the hands of a skilful foreman, it is certain to give trouble by its irregular results.

Attempts have been made to combine revolving cylinder roasters with independent smelting hearths, on which the roasted charge could be sintered or fused, as suggested by Brückner years ago; but such attempts have all been complete failures. The fact that no systematic sintering of the charge is possible in any kind of mechanical furnace is no great drawback, for the plain roasted charge can be removed in an iron hopper truck and dropped, still red hot, into a separate smelting hearth.

Shaft Furnaces.—The only furnace of this kind which has been successfully used on pyritous lead ores is the well-known *Gerstenhofer*,* which at Freiberg puts through in twenty-four hours about 60 tons of a pyritous ore containing 18 per cent. galena, 60 per cent. pyrites, and 22 per cent. gangue, and roasts it down to about 7 per cent. sulphur. Ordinary lead ores, properly so called, could not, of course, be roasted in such a furnace at all.

Muffle Furnaces.—The same remark applies to the use of

* *v.* Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 55.

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these furnaces for mixed leady ores. At *Oker* the Hasenclever* muffle furnace is employed for the first roasting of the mixed ore fines, which average 11 per cent. galena, 15 per cent. chalcopyrite, 28 per cent. blende, 25 per cent. pyrites, 14 per cent. heavy spar, and 7 per cent. of other gangue matter; simply because it is required to condense the sulphurous acid gases for the manufacture of sulphuric acid.

Summary.—As a rule, it may be said that for rich galena ores containing but little of other sulphides, except blende, there is at present, under ordinary circumstances, no alternative to the use of hand-rabbled long hearth reverberatories, for which all coarse particles should first be crushed at least to a 6, and, preferably, to an 8 or 12 mesh. If, however, labour is *very* expensive a mechanically-rabbled furnace may be advisable, the *Ropp* and *Pearce* forms being, perhaps, on account of their simplicity, best adapted to such readily fusible material. Of the two, the former is decidedly preferable.

When, however, the ore to be treated carries a larger proportion of iron pyrites than of the other sulphides, any of the mechanically-rabbled reverberatories may be employed for the ore fines, the multiple-hearth *Wethey* and *Keller* types possessing decided advantages over the others, on account of their economy of fuel, though ill adapted to the handling of readily sintered material, except with special precautions to keep down the temperature.

As regards coarse ore in which pyrites is the predominating constituent (say all over pea to nut size), it may be either crushed and roasted with the fines in a hand- or mechanically-rabbled reverberatory, or, where local conditions will permit, roasted in stalls or kilns at a lower cost, and frequently to much greater advantage. The prices of labour, materials, fuel and motive power, value of acid fumes, &c., must be duly considered, and each case decided on its merits.

It may be remarked with regard to all mechanical furnaces that they need careful handling by skilled labour, which is always expensive, and frequently not obtainable outside of great metallurgical centres. Unless, therefore, the smelting works is on a large scale and very favourably situated as regards the supply of reliable skilled labour, it is much better to depend upon the ordinary hand reverberatory for roasting all fine leady ores, even those containing so much pyrites as to render them suitable for handling in a mechanical furnace.

As an example, it may be noted that at the great *Alaska-Treadwell* mine long hand-worked reverberatories have been substituted for the *Brückner* and *Spence* furnaces formerly used for dead-roasting pyritic concentrates for chlorination simply on this ground. On this point Hamilton Smith says :—†

* *Ibid.*, p. 83. † *Trans. Fed. Inst. of Min. Eng.*, vol. vii., part i., p. 109.

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"I think the chances are that no mechanical furnace will ever prove so successful *at a mine* for perfectly roasting sulphides as a reverberatory. Sulphide ores vary from week to week. At large works, where concentrates from various mines are mixed under the charge of a competent man, it is possible that mechanical stirring may answer, but at one mine the owners cannot afford to pay very high salaries, and, consequently, the roasting foreman is generally or almost invariably a rule-of-thumb man."

If this be true as regards pyritic concentrates, it must be very much more so in the case of galena ores with their decided tendency to sinter. Only the largest and best-equipped concerns can afford to experiment with mechanical furnaces on any material containing upwards of 20 or 25 per cent. lead.

CHAPTER VII.

BLAST FURNACE SMELTING—PRINCIPLES.

Introductory.—Roasting is an indispensable preliminary to the blast furnace smelting of galena ores, but the importance of a perfect roast has greatly diminished since the introduction of the modern system of fast driving, with its enormous volume of air supplied through tuyeres of large area. In the German system of smelting with a small number of tuyeres of small size, giving a powerfully reducing effect with slow smelting, the whole of the sulphur present goes to form matte. By using a larger volume of blast, however, it is possible to burn off a considerable portion of the sulphur present, and, therefore, an imperfectly roasted charge, or even a mixture of raw and roasted ore, may be employed without much increasing the production of matte.*

Though *roast-reduction*, therefore, is the typical blast furnace process, at the present time both *reaction* and *precipitation* are in a minor degree exemplified at different centres.

Roast-reduction predominates in the (ordinary) case where the lead ores have been reduced pretty thoroughly to an oxidised condition by natural agencies or by a thorough roast. Lead is reduced to metal chiefly by the agencies of carbonic oxide and of glowing carbon; and sulphur chiefly forms an iron-lead matte, except a small portion expelled as SO_2 and another small portion carried into the slag as zinc, lead, iron, and barium sulphides. These conditions prevail at Freiberg, Mechernich, and Przibram; at Cartagena, Pertusola, and Laurium; at most of the great smelting plants in the U.S., Mexico, and at Broken Hill, N.S.W.

Precipitation predominates in the exceptional case where the lead ores are charged in an unaltered sulphide condition together

* The volatilisation loss, however, is in this case much increased.

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with oxidised iron ores and other fluxes in high furnaces, a small volume of air only being employed, together with a very high fuel consumption. The atmosphere in the furnace is powerfully reducing, and lead sulphide is acted upon by metallic iron reduced from the fluxes, producing a small quantity of iron-lead matte. The typical example of this condition of affairs is to be found at Clausthal, but it may be presumed that precipitation always comes into play to a greater or less extent when the conditions are favourable to a powerfully reducing action. The practice in the United States, until within the past few years, undoubtedly involved more or less "precipitation."

Reaction may be said to predominate in the, as yet exceptional, case when the ores are very imperfectly roasted, or when raw and roasted ores are mixed and charged in a comparatively low column into a blast furnace, the atmosphere of which is made oxidising by the expedient of supplying it with a larger volume of air than can be burnt up by the coke at the given pressure. Lead is chiefly liberated by the reaction of its sulphate and oxide upon unaltered sulphide, and the sulphur present in the charge is chiefly expelled as SO_2. This practice in its typical form is exemplified at the Block 14 Smelting Works, Port Adelaide,* but to some extent reaction, no doubt, comes into play wherever a large increase in furnace capacity has been aimed at by increasing the volume of the blast without very greatly increasing the height of the furnace. Whenever an increase of capacity obtained by this means without altering the composition of the charge is found to be unaccompanied by an increased matte fall, it is safe to reckon that some reaction effect has come into play, and this condition of affairs, though unusual, is occasionally reached at several large European and Australian lead smelting establishments.

Although, however, *precipitation* and *reaction* are always more or less concerned in blast furnace lead smelting, they play a part which is, on the whole, distinctly subordinate to the more universal *roast-reduction* process. The principles of blast furnace smelting will, therefore, be discussed chiefly on the *reduction* basis with only incidental reference to such exceptional conditions.

Objects of Blast Furnace Smelting.—The charge consists, as a rule, of both raw and roasted ores mixed in convenient proportions, a majority of the ores valuable chiefly for their silver contents being smelted in a raw condition. It may contain, besides oxide, sulphate and sulphide (sometimes silicate) of lead, silver and gold, the former combined as sulphide or native, also oxides, sulphides and sulphates of iron, zinc, and copper, arsenides and antimonides (arseniates and antimoniates), free silica

* And may be said to have originated with Mr. T. G. Greenway, the able metallurgist and manager of these works.

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and silicates of iron, alumina, lime and magnesia, barium and calcium sulphates, and also, in the raw ores, carbonates of lime, magnesia, iron and zinc, fluorspar, and other gangue minerals.

It is mixed with fuel and with appropriate fluxes and smelted, the object being to produce:—

1. A "work-lead" or "base-bullion," which shall contain as much as possible of the lead, silver, and gold present.

2. A "matte," which shall contain as much as possible of the copper, together with the rest of the lead, silver, and gold.

The remaining ingredients are to be got rid of by slagging or by volatilisation, but when much arsenic is present an additional product is formed in the shape of speiss, which complicates the extraction.

Requirements of the Ore Charge.—The ore charge should contain for good work sufficient lead to yield at least 8 to 10 per cent. (and preferably 12 per cent. or upwards) on the whole weight of charge including fluxes; and the proportion of silver should not be more than 3, or at most 4, ozs. for each per cent. of lead shown by dry assay. The other constituents of the charge—silica, iron, lime, &c.—should have been, as far as possible, balanced by mixing various classes of ore, so as to produce a "good" slag with the minimum amount of barren fluxes.

Requirements of the Slag.*—The slag produced must be good, economically as well as metallurgically. To be good *metallurgically* a slag must fulfil the following conditions:—(1) Low fusibility; (2) low contents both of lead and silver; and (3) ready separability from matte and speiss.

1. The melting point of lead slags may vary between 1030° C. (*Schetel*) and 1273° C. (*Balling*), being lowest when its composition approaches that of an iron monosilicate, and highest as it approximates to a bisilicate, especially when high in lime and magnesia.

2. According to Eilers,† when producing 300 ozs. bullion a good slag should not contain over ¾ per cent. lead (by dry assay) or ½ oz. silver (ordinary crucible assay uncorrected) per ton. These figures are, however, but rarely attained as averages on the large scale.

3. The separability from matte and speiss depends partly on the *density* of the slag (3·4 to 3·6) and partly on its *viscosity*. The author is not aware of any experimental investigations on the latter point, but it is known in a general way that siliceous slags are less perfectly fluid than those of a basic character, while both *zinc* and *magnesia* tend to render slags pasty.

* *v.* Hahn, *Mineral Resources of the U.S.*, 1882, p. 325; Iles, *ibid.*, 1883-4, p. 440; Schneider, *Trans. A.I.M.E.*, vol. xi., p. 56; Hofman, *op. cit.*, p. 133.

† *E. and M. J.*, April 9, 1881.

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To be good *economically* a slag, besides satisfying the above conditions, must permit of smelting as much as possible of the ore on which there is the largest margin of profit with the minimum of costly flux. Not only the cost of flux delivered at the works has to be borne in mind, but the cost of smelting it, for every pound of flux added to the furnace charge means a pound of ore left out. It costs about as much to smelt a ton of flux as a ton of ore, therefore great attention should be directed to utilise, as far as possible, the various kinds of ore available, so as to employ as little barren flux as possible.

Fluxes.—The fluxes used in the lead blast furnace are :—

1. *Silica* in the form of sand or siliceous silver ores, used only for basic ferruginous ores. This is not usually spoken of as "flux," that name being reserved for basic fluxing materials, and (in Colorado) for the lead ores which are added to siliceous mixed ore charges.

2. *Iron Ore* (also *manganese ore*).—This is a favourite flux for siliceous ores whenever obtainable, especially as, when derived from the gozzans of ore deposits, it usually carries more or less silver and gold, and sometimes lead. Its cost alone precludes its more universal use for simple fluxing purposes when not carrying any "values." All iron ores contain more or less silica, which, besides diminishing their fluxing power, forms an unnecessary amount of slag in the furnace. This is almost always objectionable, not only on account of the cost of smelting worthless material, but also because of the lessened furnace capacity for ore, and of the extra losses of lead and silver in this additional slag.

When smelting very zincy ores which are not too siliceous, however, it is often preferable to use a cheap siliceous iron flux rather than the more expensive high-grade iron ore, as the extra amount of slag formed assists in carrying off zinc.

Hammer scale and *puddle cinder* are still employed at Mechernich, and, perhaps, at one or two other places, but are far too expensive for use at most great smelting centres.

It is impossible too strongly to impress upon the novice that in the ordinary lead blast furnace an excess of silica lies at the root of most of the difficulties and irregularities in furnace manipulation, except those caused by zinc, and that the troubles caused by an excess of base (especially of iron) are much less to be feared than those due to an excess of silica. It is often necessary to economise iron-fluxing ores on account of their expense, or the cost of roasting, if the iron flux has to be prepared on the spot from pyritous ores, but a pretty safe rule for the inexperienced metallurgist to follow is "when in doubt or in trouble increase the iron ore on the charge."

3. *Limestone.*—This is the flux most widely used, the purest kind being the best for furnace work. Generally, however, the

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best obtainable is more or less siliceous or argillaceous, and frequently also dolomitic. Siliceous and argillaceous impurities are objectionable in exactly the same way as when found in iron ores—viz., because they bring about the formation of an unnecessary amount of slag. Magnesia, theoretically, should be more efficacious than lime for neutralising silica on account of its lower molecular weight, but, unfortunately, the silicates of magnesia are so infusible as to much more than offset this advantage, the use of very dolomitic limestones becoming on this account most objectionable.

The proportion in which lime may be used varies greatly In the practice of twenty or thirty years ago (chiefly owing to the abundance of iron ores and the cheapness with which pyrites could be roasted) limestone was but seldom added to the charge, and the slags contained but little lime. Nowadays, on the other hand, the price of iron flux being usually higher and the cost of roasting greater, a larger proportion of limestone is advantageously employed, ranging, when the zinc present is small in amount, up to 30 per cent. CaO in the slag produced. There are, however, drawbacks to its use above a certain proportion, since, although it brings down the specific gravity of the slag, it decreases its fluidity and its fusibility in a corresponding degree; and, to the extent of the decreased fusibility and of the higher specific heat which it possesses compared with the irony slags increases the fuel consumption.

On the other hand, however, a given weight of lime will neutralise more silica than the same weight of ferrous oxide, so that less total weight of slag is produced from the same quantity of silica, with smaller losses of lead and silver, and, therefore, limestone is in most cases the most advantageous flux to employ irrespective of its lower first cost.

Slags from the same or a distinct operation are frequently added as flux with one or more of the following objects:— (1) To recover lead or silver contained in them; (2) to open up a fine dense charge and prevent it from clogging the blast; and (3) to add some basic or acid constituent in which the charge is deficient.

However well a furnace is running, some slag will always be produced containing shots of matte or speiss, or otherwise too rich to throw away (so-called "foul slag"); this will generally amount to from 5 to 10 per cent. of the ore charge. Slag having been already once melted is much easier to remelt than an ore mixture containing the same constituents, therefore the addition of slag to a refractory mixture will assist it to melt more easily.

Use of Burnt Lime instead of Limestone.—Burnt lime was tried instead of limestone in the iron blast furnace with the idea that the fuel required to expel 44 per cent. of its weight

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as CO_2 would be saved. The matter was fully discussed by Bell,* who showed that burnt lime absorbs much moisture and CO_2 in the upper part of the furnace, which have to be expelled lower down; and that, even when large lumps burnt at a high temperature are used, the saving in fuel is only about 3½ per cent. The same objections do not, however, hold good in the case of lead furnaces, for the descent of the burnt lime from the charging floor to the reduction zone is too quick to admit of much absorption of CO_2, while the reduction and fusion zones of a lead furnace are so restricted that there is a very real loss of temperature and fuel in decomposing limestone in the furnace. According to Le Chatelier, calcium carbonate requires a temperature of 812° for its decomposition, and it is pretty certain that this temperature would not be reached until the limestone was nearly down to the top of the jackets—*i.e.*, close to the smelting zone where all the heat of the fuel is required for iron reduction and slag formation.

According to Bretherton,† burnt lime has been used instead of limestone at the *American* smelter (Leadville, Colo.) since 1885, with the result that the furnace runs faster, the slag is hotter and cleaner, and fewer wall accretions are formed. Other metallurgists who have tried burnt lime have found difficulties due to its friability and pulverulent condition when partially slaked, and it would seem that it is essential for the lime to be (*a*) freshly burnt, and (*b*) in large lumps of, say, 5 to 6 inches in longest dimension. When satisfying these conditions the advantages of burnt lime would seem to be as follows:—(1) No crushing or sledging required; (2) saving of fuel owing to absence of reaction between the expelled CO_2 and carbon; (3) increase of furnace capacity for ore proportional to the difference of weight; (4) no loss of heat in smelting zone, therefore hotter and cleaner slags; (5) less total quantity of gas produced in furnace, therefore less volatilisation loss; and (6) possible direct action of the porous lime in upper part of the shaft upon sulphides of Zn and Pb volatilised from smelting zone with formation of CaS, and diminution in the amount of wall accretions formed. It is to be noted that in some cases the saving in freight caused by the less weight will pay for the cost of burning.

Composition of Slags.‡—The principal slags used in lead smelting are monosilicates,§ in which the oxygen ratio of bases to silica is as 1 : 1, the general formula being

$$2RO \,.\, SiO_2 \,.\, [2R_2O_3 \,.\, 3SiO_2].$$

* *The Manufacture of Iron and Steel*, London, 1884, p. 60.

† *E. and M. J.*, March 4, 1893.

‡ An interesting attempt is made by Austin (*E. and M. J.*, January 27, 1894) to connect lead slags graphically by means of curves. The author has here attempted to refer them to formulæ.

§ Often called unisilicates.

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These are, especially when mixed, decidedly more fusible than any other combinations of silica and bases.

True bisilicates, though occasionally met with in copper smelting, are never used in lead smelting, as they carry away too much lead as silicate, besides being viscid, and causing various inconveniences in furnace working. A sesquisilicate with oxygen ratio of bases to silica as 2 : 3 is, however, sometimes made

$$\begin{Bmatrix} 2RO \,.\, SiO_2 + \\ 2(RO \,.\, SiO_2) \end{Bmatrix} \text{ or } \begin{bmatrix} 2R_2O_3 \,.\, 3SiO_2 + \\ 2(R_2O_3 \,.\, 3SiO_2) \end{bmatrix}$$

being regarded as a mixture in equal proportions of monosilicate and bisilicate. Other mixtures of mono- and bi-silicates with oxygen ratios of 4 : 5, 5 : 7, &c., are also met with.

These higher silicates all melt at a higher temperature than simple monosilicates. Besides economising flux, therefore (for which purpose they are chiefly employed), their use is indicated whenever a higher temperature is required in the smelting zone of the furnace, as *e.g.*, (1) for reducing Fe_2O_3 to Fe for use in precipitating lead from its sulphide; (2) for smelting arsenical ores, the "speiss" produced by which is liable to "freeze" unless kept very hot.

With very high proportions of zinc and of alumina, a sub-silicate or mixture of mono- and sub-silicate has to be made, in which the oxygen ratio of bases to silica is as $1 + n : 1$; n being any fraction up to about 0·5 or 0·6.

TABLE XV.—Relative Equivalence of Different Slag-forming Bases.

One part by weight of Silica requires	Parts by weight of Bases.	One part by weight of Base requires	Parts by weight of Silica.
For Monosilicates—		*For Monosilicates—*	
Ferrous oxide, . .	2·40	Ferrous oxide, . .	0·416
Manganous oxide, .	2·36	Manganous oxide, .	0·422
Lime, . . .	1·86	Lime, . . .	0·535
Baryta, . . .	5·10	Baryta, . . .	0·196
Magnesia, . . .	1·33	Magnesia, . . .	0·750
Alumina, . . .	1·14	Alumina, . . .	0·873
Zinc oxide, . .	2·70	Zinc oxide, . .	0·370
For Bisilicates—		*For Bisilicates—*	
Ferrous oxide, . .	1·20	Ferrous oxide, . .	0·883
Manganous oxide, .	1·18	Manganous oxide, .	0·845
Lime, . . .	0·93	Lime, . . .	1·070
Baryta, . . .	2·55	Baryta, . . .	0·392
Magnesia, . . .	0·66	Magnesia, . . .	1·500
Alumina. . . .	0·57	Alumina, . . .	1·747
Zinc oxide, . .	1·35	Zinc oxide, . .	0·740

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The preceding table, originally given by Balling,* shows the proportions of silica and bases required to form monosilicates and bisilicates. Baryta and zinc oxide have been added, and the figures for sesquisilicates have been omitted, since they may be regarded as simple mixtures of mono- and bi-silicates in equal proportions. Any required intermediate mixture can be readily obtained from the figures of the mono- and bi-silicates.

The following table, based primarily upon that given by Hofman, with alterations and additions, shows the composition of certain typical slags which have been used in practice with uniformly good results:—

TABLE XVI.—Composition of Typical Lead Slags.

Authority.	Oxygen ratio Bases : Silica.	SiO_2.	FeO MnO.	CaO BaO MgO.	Al_2O_3.	ZnO.	Total.	Remarks.
1. Eilers,† . .	1 : 1	28	50	12	...	...	90	
2. Eilers,† . .	1 : 1	30	40	20	...	...	90	Al_2O_3 + ZnO under 7 %
3. Schneider, .	1 : 1	33	33	24	...	...	90	
4. Raht, . . .	1 : 1	35	27	28	...	...	90	
5. Hahn, . .	4 : 5	34	50	12	...	...	96	
6. Hahn, . .	5 : 7	36	40	20	...	...	96	Al_2O_3 + ZnO under 2 %
7. Murray, . .	2 : 3	39	32	25	...	...	96	
8. Schneider, .	1 : 1	34	24	30	10	...	98	...
9. Kochler, . .	1 : 1·3	40	26	16	10	4	96	...
10. Page, . . .	1 : 1·3	33	36	16	...	7	92	Al_2O_3
11. Ropp, . . .	7 : 8	30	36	16	...	10	92	under 5 %
12. Greenway, .	1 : 1	25	33	14	3	16	91	Also ZnS 4 %
13. Lower Harz,	1·6 : 1	17	35	7	6	20	85	Also $BaSO_4$ 10 %

Seeing that any definite mixture or combination of silicates may dissolve and absorb free silica or free base, considerable variations are allowable from the above proportions,‡ especially as regards the relative proportions of iron and lime which, in non-zinciferous slags, may replace each other within wide limits. It should be borne in mind that—

Lime must vary inversely with *iron* and directly with *silica*.

Alumina must vary directly with *lime* and inversely with *iron* and *silica*.

Zinc oxide must vary directly with *iron* and inversely with *silica* and *lime*.

As regards *silica*, with ores not too high in zinc it is frequently advisable to aim at a sesquisilicate (No. 7 in the Table), espe-

* *Compendium der Metallurgischen Chemie*, Bonn, 1882, p. 98.

† When used nowadays these slags are figured 30 : 48 : 12 and 32 : 38 : 20 respectively.

‡ Except as regards No. 11, which seems peculiarly sensitive; *v.* Chap. xi.

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cially when fluxes are scarce and expensive; for although, on the one hand, the fuel consumption is increased, owing to the higher fusing point and the higher specific heat of slag containing an increased proportion of silica, yet, on the other hand, the quantity of slag produced is less, and, therefore, with the same slag assay the losses of lead and silver will be smaller; besides which the higher temperature of the molten slag assists in keeping the crucible in good condition. Slags containing over 40 per cent. SiO_2 are sometimes made, but they are somewhat viscous and retain much lead as silicate, which can only be reduced by greatly increasing the fuel consumption. With such highly siliceous slags, moreover, the rate of smelting is retarded and there is more danger of forming iron "sows" or crucible accretions.

Unless the proportion of *zinc oxide* rise above 10 per cent. the slag should not run below 30 per cent. SiO_2, as, in order to get it so low, ferruginous flux has usually to be employed, which, besides its cost, raises the specific gravity of the slag and so increases its liability to carry away, not only matte, but even lead itself. As the proportion of zinc rises, the proportion of silica may be allowed to run down to 25 per cent., and with very barytic ores to as little as 14 or 15 per cent. In ordinary circumstances, however, and with any common mixture of ores not too rich in zinc, the slags should contain between 30 and 35 per cent. silica.

Formulæ of Type-slags.—When the ores are comparatively low in zinc and alumina, so that the total of ZnO, Al_2O_3, PbO, S, &c., only makes up about 10 per cent. of the slag, leaving 90 per cent. for SiO_2, FeO (MnO), and CaO (MgO), a convenient rule is to calculate SiO_2, FeO, and CaO to 85 per cent. of the slag, adding an extra 5 per cent. SiO_2 for the 10 per cent. of bases Al_2O_3, ZnO, PbO, &c. The first four leading monosilicate types calculated thus are given in Table XVII. (the names "quarter," "half," "three-quarters" simply refer to the ratio of lime to iron, the latter being unity).

When alumina and zinc are practically absent, so that SiO_2, FeO, and CaO add up to 96 per cent., and when MgO and BaO are each under 3 per cent., combinations of monosilicates (iron) with bisilicates (lime) can be adopted advantageously without risk of making the slags pasty. The three type slags in Table XVIII. are Nos. 5, 6, and 7 of Table XVI.

Aluminous Slags.—When the ores are free from zinc or nearly so, and so aluminous as to yield a slag with 8 to 12 per cent. Al_2O_3, and when at the same time iron flux is scarcer and more expensive than limestone, type slag No. 8 (Table XVI.) first made by Schneider is the proper slag to use. It somewhat resembles No. 4 of Raht, but alumina replaces part of the iron.

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TABLE XVII.—Formulæ and Composition of Typical Lead Slags.

Formulæ.	SiO_2.	FeO.	CaO.	Total.
1. *"Quarter" Slag.*				
3 [2FeO . SiO_2], + 2CaO . SiO_2, =	30·6	55·1	14·2	100
	26	47	12	85
Add 5 per cent. SiO_2,	31	47	12	90
In practice,	30	48	12	90
2. *"Half" Slag.*				
3 [2FeO . SiO_2], + 2 [2CaO . SiO_2], =	31·4	45·2	23·4	100
	27	38	20	85
Add 5 per cent. SiO_2,	32	38	20	90
In practice,	32	38	20	90
3. *"Three-quarter" Slag.*				
2FeO . SiO_2, + 2CaO . SiO_2, =	31·9	38·3	29·8	100
	27	33	25	85
Add 5 per cent. SiO_2,	32	33	25	90
In practice,	33	33	24	90
4. *1 : 1 Slag.*				
3 [2FeO . SiO_2], + 4 [2CaO . SiO_2], =	32·3	33·2	34·5	100
	28	28	29	85
Add 5 per cent. SiO_2,	33	28	29	90
In practice,	34	28	28	90

TABLE XVIII.—Formulæ and Composition of Typical Lead Slags.

Number,	5.		6.		7.	
Formula,	3 [2FeO . SiO_2] + 2[CaO . SiO_2].		3 [2FeO . SiO_2] + 4[CaO . SiO_2].		2FeO . SiO_2 + 2[CaO . SiO_2].	
Oxygen Ratio,	4 : 5.		5 : 7.		2 : 3.	
	Theory.	Practice.	Theory.	Practice.	Theory.	Practice.
SiO_2,	35·5 = 34	34	39·0 = 38	36	41·3 = 39	39
FeO,	51·2 = 49	50	40·2 = 38	40	33·0 = 32	32
CaO,	13·3 = 13	12	20·8 = 20	20	25·7 = 25	25
Total,	100·0 = 96	96	100·0 = 96	96	100·0 = 96	96

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The formula of this slag worked out from the percentages given is $12SiO_2$, 7FeO, 11CaO, and $2Al_2O_3$, which gives:—

$$9[2(\tfrac{7}{11}Fe\ \tfrac{4}{11}Ca)O \cdot SiO_2] + 2Al_2O_3 \cdot 3SiO_2,$$

showing an oxygen ratio for the silicates of 1 : 1.

The slag produced at the *Broken Hill* works of the *Proprietary Company* (No. 9 of Table XVI.) is also highly aluminous, but it is impossible to doubt that the alumina in it plays the part of a base, as the slag, though siliceous, has not the marked physical characteristics of a bisilicate. Its formula works out as $13SiO_2$, 7FeO and MnO, 6CaO and MgO, $2Al_2O_3$, 1ZnO, which may be expressed:—

$$3[2FeO \cdot SiO_2] + FeO \cdot ZnO \cdot SiO_2 + 6[CaO \cdot SiO_2] + 2Al_2O_3 \cdot 3SiO_2,$$

or,

$$4[2RO \cdot SiO_2] + 6[RO \cdot SiO_3] + [2R_2O_3 \cdot 3SiO_2],$$

showing an oxygen ratio of 1 : 1·3.

With still larger proportions of alumina and much less silica, the former behaves as an acid, and monosilicate aluminate slags are formed. Thus, another slag made by Schneider contained SiO_2 20 per cent., FeO 36 per cent., CaO 25 per cent., and Al_2O_3 15 per cent. = 96. Working out the formula from these percentages we have $11SiO_2$, 17FeO, 15CaO, and $5Al_2O_3$, corresponding to a simple monosilicate, in which part of the silica is replaced by alumina, thus:—

$$2(\tfrac{11}{17}Fe\ \tfrac{15}{17}Ca)O \cdot (\tfrac{11}{17}SiO_2\ \tfrac{5}{17}Al_2O_3),$$

or more simply,

$$FeO \cdot CaO \cdot (\tfrac{2}{3}SiO_2\ \tfrac{1}{3}Al_2O_3).$$

According to Hahn,* alumina always acts as a base, but almost all metallurgists (including Iles,† Schneider,‡ Henrich,§ and Hofman‖) are now of opinion that it plays the part of an acid in slags with a low percentage of silica. It would appear that first the strongest base (iron) saturates itself with silica, next the lime, and then if there is sufficient silica left over it will form a silicate of alumina, while if silica is deficient the alumina combines with part of the lime to form an aluminate. When the percentage of silica present is just sufficient to form monosilicates of iron and lime, the acidity or basicity of alumina will be determined by exterior or accidental conditions, such as the relative amounts of other bases present, temperature, percentage of sulphur, &c. The exact position of the "neutral zone," as we may call it, between acidity and basicity of alumina may correspond with higher or lower percentages of silica, according as the slags are richer in lime or in iron; generally speaking, for any given percentage of silica, slags rich in lime will bear more alumina than those rich in iron.

* *Mineral Resources of the U. S.*, 1882, p. 328. † *Ibid.*, 1883-4, p. 433.
‡ *Trans. A.I.M.E.*, vol. xi., p. 59. § *E. and M. J.*, Dec. 27, 1890.
‖ *Metallurgy of Lead*, p. 143.

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Zinciferous Slags.—When the proportion of *zinc oxide* is from 4 to 8 per cent. it may replace lime in any of the four monosilicate slags, 10 parts ZnO being equivalent in neutralising power to 7 parts CaO. In practice some metallurgists reckon that each 5 parts ZnO require the lime to be reduced by rather more than an equal amount, and the iron augmented to correspond. In this way the "three-quarter" slag No. 3 (with SiO_2 33, FeO 33, CaO 24, and ZnO, perhaps, 1 or 2 per cent.) becomes No. 10 (Table XVI.) (SiO_2 33, FeO 36, CaO 16, ZnO 7) when running on zincy ores. It is better, however, to diminish the silica also; thus, slag No. 11 (Table XVI.) is a very good one for zincy ores, its formula being $3[2RO \cdot SiO_2] + CaO \cdot SiO_2$, in which R is $\frac{4}{5}Fe\,\frac{1}{5}Zn$.

When the proportion of zinc oxide rises above 10 per cent., all ordinary slags become pasty and tend to form accretions above the lead. With a monosilicate slag, according to Hofman, "16 per cent. is the maximum of zinc oxide with which it is possible to run, and this very soon closes up the crucible," but Greenway has found that over 20 per cent. of zinc oxide can be run without difficulty, provided the slag be rich in iron and that SiO_2 and CaO are kept within very narrow limits, those for the former being between $23\frac{1}{2}$ and 26 per cent., and for the latter between 12 and 16 per cent. This is very easy when zinc-lead ores are accompanied by much pyrites which serves as a flux after roasting, but where pyrites is conspicuously absent, as at Broken Hill, it is necessary to use a good deal of barren iron ore.

Slag No. 12 (Table XVI.), produced at the *Broken Hill Block 14 Smelting Works*, leaving out the ZnS and PbO present, yields on calculation the proportions $42SiO_2$, 40FeO, 6MnO, 20ZnO, 25CaO, and $3Al_2O_3$, corresponding with the formula of a monosilicate in which part of the silica is replaced by alumina, and may be written as follows:—

$$20[2FeO \cdot SiO_2] + 10[2ZnO \cdot SiO_2] + 12[2CaO \cdot SiO_2] + 3[2MnO \cdot Al_2O_3],$$

or more simply,

$$2[2RO \cdot SiO_2] + [2R^1O \cdot (\tfrac{4}{5}SiO_2\,\tfrac{1}{5}Al_2O_3)],$$

in which R is $\frac{2}{5}Fe\,\frac{1}{5}Zn$ and R^1 is $\frac{4}{5}Ca\,\frac{1}{5}Mn$.

Slag No. 13 (Table XVI.), made at the smelting works near *Goslar* (Harz), averages only 17 per cent. SiO_2 and, neglecting the $BaSO_4$ in solution, corresponds very nearly with the formula:—

$$4[3RO \cdot SiO_2] + x[RO \cdot Al_2O_3].$$

Physical Properties of Lead Slags.—The specific gravity of slags has been already referred to. According to Iles, the average specific gravity of one hundred good slags was 3·691

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and, as a general rule, 3·4 to 3·6 may be considered as the practical limits of ordinary slags. Seeing that ordinary lead-mattes run from 5·0 to 5·3, the margin for separation is a narrow one.

Melting Point.—Schertel determined the melting point of Freiberg (ferruginous) lead slag to be 1073° C. Iles has lately* conducted some experiments on lead slags by the method of mixtures, using pieces of steel placed in the slag run, and comes to the conclusion that the average temperature of slag from a furnace in good work is about 2000° F. (1094° C.). The same author quotes Goetz as having found the specific heat of lead slag to be 0·18, and its melting point 2012° to 2156° F. (1060° to 1180° C.), which confirms the above result. Iles emphasises the fact, well-known to all smelters, that the temperature of the slag varies to a great extent independently of the percentage of fuel used, a higher percentage of fuel by no means always giving a hotter slag.

It might be supposed that a low melting point would always be a most desirable quality, but this is by no means the case. The quantity of fuel required per ton of ore is, indeed, less in proportion as the slag is more fusible, but (since the temperature before the tuyeres can never rise much above the melting point of the slag) both the reducing power of the furnace and the separating power of matte from slag are less in proportion to the lower temperature of the slag. Besides the cost of fluxes, therefore, the necessity of securing sufficient reduction, and a sufficiently clean separation of matte, interfere to some extent with the formation of the most fusible slag possible.

All slags when cooling pass through a viscid stage before solidifying, though, in the case of a well-proportioned slag of definite composition, the change from the perfectly liquid to the solid condition is comparatively sharp and well marked. Hence, even a good slag may appear thick or viscid, if the furnace is running "cold" from any cause, such as a slight deficiency of fuel or wet charges (and especially wet coke). In such a case it is necessary to charge in more fuel. Generally speaking, slags high in silica or alumina and lime are less perfectly fluid when hot than those high in iron; the former also soften much below the melting point, whereas basic irony slags, which are perfectly fluid above their melting point, set and become strong immediately they cool below this point.

Crystallisation.—Most slags crystallise more or less completely in cooling, the crystallisation becoming more perfect as the rate of cooling is slower. When suddenly chilled, as in the operation of sampling (best performed by dipping a clean ⅜-inch iron rod into each slag pot, withdrawing, and plunging quickly into a deep vessel of water), lead slags remain in a vitreous condition, and are quite brittle. When cooled more slowly, on the other

* *S. of M. Q.*, vol. xvii., pp. 20-25.

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hand, they become tough and more or less crystalline. Acid slags are more glassy than the basic varieties, and slags high in alumina and lime remain in a vitreous condition longer than those high in iron and zinc; the latter element in particular has a strong tendency to produce stony slags. It should be borne in mind that the crystals which develop in the centre of a cooled slag cone are very different in composition to the crypto-crystalline matrix surrounding them.

REACTIONS OF THE LEAD BLAST FURNACE.

Reduction and Reducing Agents.—The principal reducing agents in the lead blast furnace under ordinary conditions are **carbon and carbonic oxide**; under exceptional conditions **sulphur, iron,** and metallic sulphides also act as reducing agents.

Carbon acts directly on metallic oxides at the bright red heat of the smelting zone, the product being carbonic acid with easily reducible oxides, and carbonic oxide with those which are more refractory.

$$2PbO + C = Pb_2 + CO_2.$$
$$FeO + C = Fe + CO.$$

The carbon of the fuel burnt before the tuyeres at a white heat is converted chiefly into CO_2, as proved by Schertel,* but a certain proportion is burnt directly to CO. Of the CO_2 formed a portion is reduced to CO by contact with glowing fuel in the centre of the furnace. A few inches above the tuyeres, therefore, the furnace gases contain a large proportion of CO.

Carbonic Oxide.—The carbonic oxide present in the furnace gases immediately above the tuyeres cannot, however, exert any action till it rises to a point where the temperature is less than 1200° C., because it can only reduce by self-oxidation to CO_2 a gas which begins to dissociate at that temperature. Hence the reducing action of carbonic oxide commences some little distance above the tuyeres. It acts by production of CO_2 as follows:—

$$PbO + CO = Pb + CO_2.$$
$$Fe_2O_3 + CO = 2FeO + CO_2.$$

The amount of CO_2 in the furnace gases is also increased by the decomposition of carbonates contained in the ore and fluxes, which takes place above the smelting zone. The decomposition temperatures of the ordinary carbonates found in smelting charges are as follows:†—$PbCO_3$ under 200° C.; $MgCO_3$, 650° C.; $FeCO_3$, 800° C.; $CaCO_3$, 850° C.‡

According to Iles,§ the temperature of the escaping gases from lead blast furnaces in good work may range up to 334° F., but the average is only 214° F. (101° C.). Schertel analysed nineteen

* Wagner's *Jahresberichte*, 1880, p. 188. † Hofman, *op. cit.*, p. 206.
‡ According to Le Chatelier, 812° C. § *S. of M. Q.*, vol. xvii., p. 19.

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samples of gases from Freiberg blast furnaces, and found on an average three times as much CO_2 as CO, besides small quantities of hydrogen and of marsh gas. Some of these analyses are given in Part ii., Chap. xv.

Conditions Favourable to Reduction.—The burning of carbon to CO or CO_2 is largely influenced by the shape of the furnace and by the area of the tuyeres. A distinct contraction of the furnace at the tuyere zone (bosh) is accompanied by a much more rapid descent of charge there, and, consequently, by the accumulation of a thicker layer of glowing fuel between the liquid slag and the unmelted charge. The CO_2 produced before the tuyeres in its ascent has to pass through this layer of coke, and so becomes converted into CO before reaching the unmelted charge. During its slow passage upwards through the constantly increasing width of charge, the CO has ample opportunity to become oxidised to CO_2 by absorbing oxygen from the ore which it reduces. In the case of a furnace with vertical sides, however, the layer of glowing coke is thinner and its temperature is lower, because the heat is less concentrated; the CO_2 formed, therefore, largely remains as such.

Similarly, small tuyeres deliver streams of air, which are rapidly and completely absorbed by the glowing coke in their path to form CO, while the quantity delivered by a large tuyere is so great that the oxygen is largely in excess of the available carbon at any point close in front of the tuyere; hence combustion takes place almost entirely with the formation of CO_2, which in its passage upwards through the thin bed of glowing coke has no time to be converted into CO.

Another factor which influences the reducing action of the furnace is the blast pressure. A powerful blast forces its way to the centre of the furnace, where both any oxygen unconsumed on the way and the CO_2 formed by the combustion find themselves surrounded by an excess of glowing carbon and are rapidly converted into CO, which then rises through the charge, exerting its reducing effect on the metallic oxides. A weak blast, on the contrary, penetrates the charge with difficulty. Such portion as reaches the centre is, of course, converted into CO, but a large part is burnt to CO_2 in the immediate neighbourhood of the tuyeres, and rises through the charge, together with any oxygen which has escaped burning without being reduced by the fuel. In this way, although there is reduction in the centre, oxidising effects predominate all round the shaft.

Very small charges again, which bring about an intimate admixture of fuel and ore in the furnace, increase the reducing action; while the use of large charges results in fuel and ore reaching the smelting zone successively instead of together, and to that extent is not so favourable to reduction. Similarly, a fine-ore charge hinders the draught, and causes the furnace gases

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to become more thoroughly disseminated through the ore column, so exercising a very thorough reducing action; whereas with a coarse charge a considerable portion of the blast can escape through open channels without exercising any reducing influence on the bulk of the ore.

The rapidity with which coke can be burnt in a furnace of given area with tuyeres of given size, and, therefore, the rate of smelting, depend upon the pressure of the blast, and any increase in this demands a corresponding increase in the height of the column of charge, in order to avoid waste of heat at the top. High pressure, therefore, and high furnaces mean rapid driving, especially when combined with a large tuyere area.

The following conditions are favourable to a powerful reducing effect :—

1. High column of charge.
2. Contracted tuyere zone (boshed furnaces expanding upwards).
3. Small tuyeres.
4. Small volume of blast at a high pressure.
5. Small charges of moderately fine ore.

Exactly the opposite conditions—viz., low column of charge, straight-sided furnaces, and a large number of tuyeres of large area supplying a great volume of air at low pressure to large charges of coarse material—produce an atmosphere which may be neutral or even oxidising in its effects.

"Tuyere Ratio" and "Tuyere Efficiency."—It is unfortunate that the habit of running furnaces from one general blast main, coupled with the use of the cheap and convenient so-called "positive blower," have rendered it impossible hitherto to ascertain, with any approach to accuracy, the volume of air which is supplied to any furnace, and on this account it is not possible to properly investigate the character of the work done inside the furnace under given conditions.

In the absence of satisfactory data as to the volume of air supplied, it is convenient, for the sake of comparing furnaces of different sizes, to make use of certain relations between the tonnage of ore smelted, the sectional area of the furnace at the tuyere level, and the total area of the tuyeres. The number of tons of material smelted in twenty-four hours per square foot of sectional area may be called, as first suggested by Lang, the "hearth activity," or "**nearth efficiency**," of the furnace; this will be affected not only by the volume of air supplied, but also by its pressure.

As no data are obtainable in most cases with regard to the volume of air supplied, it may be assumed to be, for any given height of charge-column, roughly proportional to the total area of the tuyeres. The number of square inches of tuyere area provided for every square foot of effective sectional area between

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the tuyeres may be conveniently termed the "**tuyere ratio**" of the furnace. With any given size of furnace and fixed "tuyere ratio," the quantity of ore smelted in twenty-four hours will be directly proportional to the pressure of blast. The number of tons smelted in twenty-four hours per square inch of tuyere area may therefore be called the "**tuyere efficiency**" of the furnace. The "**hearth efficiency**" of any given furnace will thus be the product of the volume factor, "**tuyere ratio**," into the pressure factor, "**tuyere efficiency.**" These factors are all worked out for the furnaces, details of which are given in a subsequent table, as well as for the furnaces smelting silver ores without lead, described in Part ii., Chaps. xiv., &c.

Both "tuyere ratio" and "tuyere efficiency" are of the utmost importance as affecting not only the capacity of the furnace, but also the quantity of matte produced from a given charge and the possibility of smelting imperfectly roasted ores, and they will be again referred to in subsequent chapters.

Composition of the Ore Charge.—The composition of various lead ores before roasting has been given in Table XII., page 75; and the following Table XIX. gives the composition of certain roasted lead ores as well as of two "natural carbonate" ores added for comparison.

Reactions of the Ore Components.—Some raw ore being added to the roasted ore the chemical composition of the ore charge is often very complex. The different substances present behave as follows:—

Lead oxide in powder or in porous lumps is partly reduced in the upper part of the furnace direct to metallic lead by carbonic oxide. Slagged or sintered masses are, however, impermeable to the furnace gases, and their reduction is only effected in the smelting zone by direct contact of the drops of molten oxide with glowing fuel.

Lead silicate is unaffected by CO, and even by contact with glowing carbon, except in the presence of a more stable base; basic lead silicates only give up a part of their lead, leaving an acid silicate. This is, however, readily decomposed by FeO, and at a much higher temperature by CaO also, and the PbO set free is reduced to metal by hot coke. The ferrous oxide acts equally well whether in a free condition, reduced from ferric oxide in raw or roasted ore, or combined with silica, from which combination lime will set it free in the smelting zone. In ordinary lead furnaces more or less metallic iron is reduced from its oxide in the hottest part of the furnace in contact with glowing coke, and this iron acts as a powerful reducing agent for the liberation of lead from both oxide and sulphide.

In connection with an excess of lime or other base, the sulphides of iron, calcium and barium, may act as reducing agents. These sulphides may be formed by reduction of their

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TABLE XIX.—Analyses of Ores for Blast Furnace Smelting.

	Roasted Sulphides.							Carbonates.	
	Freiberg, Saxony.	Mechernich, Rheniah Prussia.	Rodna, Transylvania.	Goslar, Lower Harz.	Pueblo, Colorado.	Mine La Motte, Mo., "Galena."	Mine La Motte, Mo., "Sulphides."	Eureka, Nevada.	Red Mountain, Colorado.
Reference,	1.	2.	3.	4.	5.	6.	7.	8.	9.
PbO,	22·00	66·85	58·44	10·02	7·91	77·40	21·86	35·65	18·40
Ag,	0·13	0·01	0·06	0·01	0·06	...	...	0·09	0·44
CuO,	0·30	0·17	0·02	0·93	3·22	...	7·04	0·15	...
ZnO,	20·00	0·19	1·03	23·64	0·98	und.	und.	2·37	1·23
Fe_2O_3,	33·30	0·78	34·37	13·62	80·39	4·31	34·37	34·39	17·12
MnO,	...	...	...	...	0·93	...	...	0·13	0·59
NiO and CoO,	...	0·10	...	...	...	1·11	4·69	...	...
Sb,	...	0·08	0·03	...	tr.	...	...	0·25	...
As_2O_5,	1·10	...	0·04	...	0·86	...	...	6·34	...
Al_2O_3,	1·80	4·24	0·23	7·16	...	und.	und.	0·64	6·08
CaO,	2·00	1·18	tr.		3·22	2·25	3·28	1·14	1·70
MgO,	0·50	...	tr.		...	...	1·45	0·41	...
$BaSO_4$,	...	...	...	20·87	...	...	...	...	...
SiO_2,	17·40	22·77	0·80	11·00	3·21	2·80	7·10	2·95	41·63
SO_3,	tr.	und.	2·25	8·62	...	...	...	4·18	3·87
S,	3·60	0·60	2·72	0·38	1·01	7·12	8·31	...	...
CO_2,	...	...	...	...	...	...	...	10·90	2·39
H_2O,	...	...	...	...	...	...	...		6·75
	102·13	96·96	96·25	96·25	101·79	...	...	100·52	100·20
Ag, oz. per ton,	42·50	3·4	19·9	4·25	20·0	...	...	30·74	143·4
Au, oz. per ton,	...	...	...	...	...	...	...	1·96	0·23

References.—1. *Oesterreichisches Jahrbuch*, vol. xvi., p. 397. 2. *Berg-und Huttenwn. Zeitung*, 1875, p. 129. 3. *Oesterr. Jahrb.*, vol. xxix., p. 27. 4. Schnabel, *Handbuch der Metallhüttenkunde*, vol. 1., pp. 329 and 389. 5. Hofman, *Metallurgy of Lead*, p. 260. 6 and 7. Kemp, *School of Mines Quarterly*, vol. ix., p. 216. 8, Curtis, *Mon. U.S. Geol. Survey*, vol. vii., 1884, p. 60. 9. Kedzie, *Trans. A.I.M.E.*, vol. xvi., p. 570.

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respective sulphates or by the action of pyrites on the bases, and their mode of action is as follows:—

$$2FeS + 4CaO + 3Pb_2SiO_4 = Fe_2SiO_4 + 2Ca_2SiO_4 + 3Pb_2 + 2SO_2.$$

Lead sulphide is acted upon in the hottest part of the furnace by metallic iron, or by mixtures of ferrous silicates with carbon, and reduced to metal with formation of ferrous sulphide, but the reaction is never complete, some lead always remaining as sulphide in the matte—

$$2PbS + FeO + C = Pb + PbS \,.\, FeS + CO.$$

Percy gives* an equation, according to which the presence of carbon is not necessary to the reduction of PbS by means of iron silicate, thus,

$$3(2FeO \,.\, SiO_2) + 5PbS = 4FeO \,.\, 3SiO_2 + 2(PbS \,.\, FeS) + 3Pb + SO_2,$$

the monosilicate becoming a sesquisilicate which has no further action upon PbS. At a higher temperature more lead can be expelled from the matte by the action of fresh iron, so that the proportion of lead in the matte varies almost entirely with the temperature. Berthier stated that lime also reduced lead from its sulphide, but, according to the experiments of Jordan,† there is no action between the two bodies at any temperature, whether in presence of carbon or not.

A certain proportion of lead is always liberated from lead sulphide above the smelting zone by reaction with oxide and sulphate, according to the characteristic equations given in Chap. ii. In some cases this reaction may become of the very highest importance, and nearly the whole of the sulphur present in the charge, even when amounting to 8 or 10 per cent., may be expelled as SO_2 almost without any formation of matte. The conditions upon which this reaction depends have been already touched upon in this chapter, and will be further discussed in connection with the description of *Block 14 Works* (Port Adelaide).‡

Finally, lead sulphide may be reduced to metal by the direct action of zinc vapours (themselves arising from the reduction of oxide in contact with carbon) producing zinc sulphide.

It is to be noted that most of the lead lost by volatilisation is in the condition of sulphide, as shown by the analyses of lead fume from blast furnaces run with a cold top.

Lead sulphate behaves in several ways. Usually the largest part reacts upon lead and other sulphides above the smelting zone, liberating metallic lead and SO_2. Another portion is probably reduced to PbS, and a third portion, in contact with free silica or with acid silicates, is converted into lead silicate;

* *Metallurgy of Lead*, p. 59. † Quoted by Percy, *op. cit.*, p. 55.
‡ *v.* Chap. xi.

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the lead sulphide and silicate thus formed are acted upon as above described.

Ferric oxide and **magnetic oxide** are reduced by CO to FeO, which combines with silica to form the basis of a slag. In the smelting zone, part of the iron is still further reduced to metal, which then decomposes lead sulphide, as already explained.

Ferrous sulphate can hardly exist in large proportion, but when present in roasted ore is decomposed to Fe_2O_3 and SO_3.

Ferrous sulphide in an ore charge chiefly runs through the furnace unaltered; part of it, however, may undergo the double decomposition with lead silicate already described on the preceding page.

Pyrites, FeS_2.—It is sometimes reckoned that pyrites, when added in the form of raw ore to the furnace charge, consumes an equivalent quantity of metallic iron, according to the equation—

$$FeS_2 + Fe = 2FeS.^*$$

Others, again, have supposed, with more reason, that one atom of sulphur is given off in the upper part of the furnace, FeS_2 thus becoming FeS. According to the experiments of Valentine,† pyrites does not give off as much as one atom of sulphur when heated in a current of furnace gases (N, CO, CO_2). After one hour's exposure to a temperature of 1250° F. the residue still contained 37 per cent. S, showing that only a little over one-third had been volatilised; the greater portion of this, moreover—viz., 12 per cent. (23 per cent. of the total sulphur present)—was expelled in the first ten minutes. It seems probable that with charges rich in pyrites from a fourth to a third of the S would be expelled at a temperature of 500° C., or sufficiently below that at which Fe_2O_3 begins to be reduced to metal, and that, therefore, at most only one-fourth instead of one-half the contained sulphur has to be reckoned as an iron consumer.

According to Henrich,‡ pyrites may act directly upon lead sulphate, just as in the experiments of Percy it was found to act directly upon PbO. In the case described, so-called "carbonate" ores (consisting chiefly of anglesite) were smelted direct with pyrites containing silver, and very little matte was produced, most of the sulphur seeming to be burnt to SO_2. Henrich gives the reaction as—

$$2FeS_2 + 5PbSO_4 + SiO_2 = 5Pb + FeSiO_4 + 9SO_2.$$

As a matter of practical experience it is found that with pyritic ores the amount of sulphur expelled is largely a matter of blast and of the speed at which the furnace is run, slow running generally diminishing, and fast driving increasing, the proportion

* Hofman, *Metallurgy of Lead*, p. 145.
† Desulphurisation of iron ores, *Trans. A.I.M.E.*, vol. xviii., p. 78, &c.
‡ *E. and M. J.*, Sept. 22, 1893.

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of matte produced from a charge with fixed percentage of sulphur, other conditions remaining the same.

Manganese oxides are reduced to MnO and enter the slag. Manganous oxide can replace ferrous oxide in all proportions, the slag being somewhat more fusible and even cleaner than iron slags. Church* in smelting carbonate concentrates at *Tombstone* (Ariz.) to a 314-oz. bullion, produced slag of the following composition :—

SiO_2	FeO	MnO	CaO	MgO	Al_2O_3	Pb per cent.	Ag oz. per ton.
29·60	11·56	43·25	7·50	trace.	6·34	1·4	trace.

He notices one defect of slags rich in manganese, which is their very slight power of taking up sulphur and other impurities, such as speiss, (probably also barium and other sulphides). Pearce† also refers to the oxidising power of manganese on blende, giving a case of a slag produced in smelting silver-copper ores in a reverberatory furnace which contained SiO_2 48 per cent., MnO 30 per cent., ZnO 12·5 per cent., while 3 per cent. of Mn also entered the matte. He points out that the presence of a large percentage of manganese in the slag ensures all the available sulphur going into the matte, and that so long as any manganese is present in the latter the copper is safe from slagging.

Chalcopyrite in raw ore loses about one-fourth of its sulphur, and melts down into a "matte"; other copper sulphides enter the matte unchanged.

Cuprous and Cupric Oxides.—The affinity of copper for sulphur being greater than that of any other metal, it passes into the matte, provided there be sufficient sulphur present; otherwise it will be reduced to metal and alloy with the lead. In order to get a perfect separation of copper in matte, however, the slags must not be too ferruginous, for with very ferruginous basic slags some of the sulphur is taken up by iron in the slag, and an equivalent proportion of copper goes into the lead. Slags fairly high in lime, therefore, give cleaner lead when running on coppery ores.

The formation of cuprous sulphide from the oxide may take place in two ways. Either the oxide may be first reduced by CO and carbon to metal, which then acts upon ferrous sulphide, or a double decomposition may take place direct with the ferrous sulphide without previous reduction, according to the reaction :—

$$4CuO + 2FeS + SiO_2 + C = 2Cu_2S + 2FeO \cdot SiO_2 + CO_2$$

If the copper oxide is first reduced to metal, the reaction may be—

$$2Cu + 2FeS = CuS + Fe \cdot FeS.$$

The metallic iron liberated and dissolved in the excess of FeS is at once disposed of by reaction upon lead sulphide or upon

* *Trans. A.I.M.E.*, vol. xv., p. 612. † *Ibid.*, vol. xi., p. 59.

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ferric oxide. Some have supposed the existence of a subsulphide of iron with the formula Fe_2S, but no definite body of the kind has yet been prepared, and the principal reason for assuming its existence is that the sulphur in lead mattes is frequently insufficient in quantity to satisfy the metals. On the other hand, metallic iron is sometimes found in mattes and it is more reasonable to suppose that it exists dissolved in the hot matte, just as copper undoubtedly exists dissolved in the regulus known as "pimple metal" when hot, though it separates out on cooling.

Arseniates are partially decomposed by heat, especially in presence of pyrites, the arsenic being to a small extent volatilised as As_2O_3 and partially reduced to arsenides. In small proportion these arsenides are carried away, partly into the slag and partly into the matte (a trace only entering the work-lead); but when the proportion is at all high an iron speiss is formed, which contains notable amounts of Pb, Cu, and Ag, and from which these substances can only be recovered with difficulty and at some considerable expense. Such portion of the arsenic as may become volatilised carries with it into the fume both lead and silver, thus increasing the volatilisation losses of these metals. By far the larger part of the arsenic, however, if any great quantity is present, combines with metallic iron to form speisses of various compositions, the most common being Fe_5As_2 and Fe_6As_2. Arsenic in a smelting charge, unless *very* small in amount, should be calculated to Fe_5As_2.

With very arsenical ores it is advisable to make slags which are high in lime and somewhat more acid than the monosilicate type, even a sesquisilicate (No. 7 of Table XVI.) being sometimes used in order to keep the temperature of the pool of slag above the crucible as high as possible, and so prevent chilling of the speiss.

Antimony has less tendency than arsenic to form speiss but quite as much to volatilise, carrying with it lead and silver, while it possesses the additional disadvantage of readily alloying with the work-lead, its separation from which introduces complications in the refining process. Antimonial speisses, when formed, always contain copper, and rarely much iron, unless arsenic be also present; they absorb more silver than arsenic speiss.

Antimoniates are reduced to antimonides, which then chiefly dissolve in or become alloyed with the lead, though a portion may enter the speiss or matte.

Antimony sulphide behaves in the main like lead sulphide, except that a much larger proportion is volatilised. The antimony reduced by metallic iron alloys with the lead, that portion, however, which is volatilised and converted into oxide carries away with it notable quantities of lead and silver.

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Gold and Silver, in whatever condition present, are reduced to metal, and alloy mainly with the lead. A smaller proportion of the silver, however, passes into the matte (chiefly owing to incomplete decomposition of silver sulphide), and a still smaller proportion into the speiss, if any is made. Traces of gold always accompany the silver, but the concentration of this metal in the lead is much more perfect than that of silver. Some silver is volatilised, but the amount is usually inconsiderable, unless haloid compounds of silver are present in the ore.

Alumina is generally unimportant in lead ores, but, as already seen, it sometimes becomes necessary to figure it as an essential part of the slag. Reference has been already made to the part played by alumina in slags high in lime and low in silica.

Magnesia in a lead ore is calculated to lime, but it does not replace lime so efficiently, magnesian slags, besides requiring a higher temperature to melt them, being always streaky and more or less "mushy." According to Hofman,* "magnesia and zinc oxide appear to intensify each other's property of being difficult to slag. In a slag with 8 per cent. Zn and 2 to 3 per cent. BaO, even 2 or 3 per cent. of magnesia shows a decidedly bad effect, and 5 per cent. causes a great deal of trouble." Magnesia appears, however, to be not nearly so objectionable in slags with high alumina—perhaps on account of the formation of spinel.

Lime decreases the specific gravity of a slag and raises its specific heat. Slags rich in lime, therefore, separate from matte more readily than irony slags, and do not chill so quickly; on the other hand, they melt only at a high temperature and require a somewhat larger amount of fuel. To a limited extent lime at a high temperature can act directly on slag already formed, expelling PbO and CuO from their silicates and assisting to produce a clean slag.

According to Schneider,† lime, besides acting as a strong base, diminishes the amount of matte formed in the furnace, and also the amount of lead going into the matte; this he explains by the formation of calcium sulphide, which is carried away by the slag in igneous fusion. The experiments recorded by Percy‡ would seem to contradict this view, which is, however, held by many experienced metallurgists.

Calcium sulphate in the ore-charge with a reducing atmosphere and basic slags is partly reduced to calcium sulphide, which is removed in the slag as above. With acid slags, SO_3 is expelled and practically all of the lime slagged as silicate.

Barytes is partly reduced to barium sulphide by contact with carbon, and partly through the action of FeS or metallic iron converted into barium silicate, which, though itself compara-

* *Op. cit.*, p. 141. † *Trans. A.I.M.E.*, vol. xi., p. 58.
‡ *Metallurgy of Lead*, p. 55.

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tively infusible, forms with iron very fusible double silicates. The reactions are—

$$3BaSO_4 + 4SiO_2 + FeS = 3BaSiO_3 + FeSiO_3 + 4SO_2$$
$$BaSO_4 + 2SiO_2 + Fe = BaSiO_3 + FeSiO_3 + SO_2.$$

It is probable, however, that most of the baryta in lead slags exists in the condition of $BaSO_4$, for slags high in BaO leave a large residue of $BaSO_4$ when decomposed with HCl. Such is certainly the case with the very basic slags of Julius and Sophien-hütte near Goslar (Harz) already referred to.

Under appropriate conditions BaS also enters the matte; thus the mattes made under very exceptional circumstances in the Altai for the past forty years have carried from 15 to 20 per cent. barium, the slags being very siliceous, and carrying 5 to 15 per cent. BaO.*

Fluorspar is not of very common occurrence in lead ores, but its extreme fusibility renders it a valuable flux when it happens to occur as gangue matter. It possesses also the useful property of assisting in the fluxing of calcium and barium sulphates, and their being carried away in the slag in that form.

Zinc oxide in the roasted ore chiefly goes into the slag, for, although simple silicates of zinc are very infusible, the basic double silicates, which zinc forms with iron and in a less degree with lime and baryta, melt with comparative ease, although the latter are always somewhat pasty. If the proportion of zinc is more than about 8 per cent. in a high lime slag, or 16 to 20 per cent. in a slag carrying 12 to 15 per cent. lime, it becomes pasty and so heavy as not to separate readily from the matte.

A considerable proportion of the zinc oxide escapes slagging and is reduced by CO in the smelting zone to metallic zinc vapours, which, together with those liberated from zinc sulphide by the agency of metallic iron, ascend with the furnace gases and condense in the upper part of the furnace. Part of the zinc vapour is re-oxidised by CO_2 at a temperature slightly below that at which it was reduced by CO, and another part in contact with SO_2 and carbon may be reconverted into sulphide. The resulting mixtures of metallic zinc, oxide and sulphides of zinc and lead in variable proportions, which condense on the walls (the so-called wall accretions), form exceedingly tough masses most difficult to detach. If not "barred off" in time, they continue to grow, contracting the sectional area of the shaft, and interfering with its regular working so much as to compel the furnace to be blown out.

Such portion of the vaporised zinc as may escape condensation is re-oxidised in the cool upper part of the furnace and carried into the flue dust as oxide or sulphate.

* Crookes and Röhrig's translation of Kerls' *Metallurgy*, vol. i., pp. 163 *et seq.*

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Zinc sulphide is much more objectionable than the oxide, for it passes in much smaller proportion into the slag and renders it much more pasty. It is important, therefore, to roast blende ores whenever possible before smelting; but even if this be done some zinc always remains as sulphide and a certain proportion will be found in much of the ore treated raw. Zinc sulphide in the charge passes in about equal proportions into the slag and into the matte, rendering both pasty and much less fusible, and carrying away into both matte and slag some of the silver which ought to follow the lead. The pastiness of both matte and slag much increases the difficulty of separating them, and gives rise to the production of quantities of foul matte-bearing slag which has to be resmelted.

When the conditions favour powerful reduction, some of the zinc sulphide is acted upon by metallic iron in the hottest part of the furnace with the production of vapour of metallic zinc, which, together with that reduced from the oxide, goes to choke up the cooler part of the furnace.

Zinc in large quantity, therefore, not only increases the difficulty of working the furnace, owing to the pastiness of slag and matte which it causes and the wall accretions which it forms, but actually increases the losses of silver and lead in slags, matte, and flue dust. Unfortunately, blende is the commonest associate of galena and, therefore, the two minerals should be as far as possible separated before the latter is submitted to the smelting process. To some extent this can be done by dressing operations, but the separation is at best imperfect entailing much loss of lead and silver in slimes, besides which the blende itself commonly carries a notable proportion of gold and silver, and there always remains a good deal of a "middle product" containing both lead and zinc.

It being, therefore, in a majority of cases impracticable to completely separate the zinc from the lead before roasting, a good deal of attention has been devoted to its separation from the roasted ore before the smelting operation. The various methods for doing this will be found described in Chap. xiv. It should be borne in mind, however, that slags containing up to 16 per cent. of zinc, if properly composed, can be handled without much difficulty.*

FUELS EMPLOYED.

The fuels best suited to blast furnace treatment are **coke** and **charcoal**, either used together or separately in various proportions. **Coal** and **wood** have been tried as partly replacing coke, and the result of experiments in their use will be detailed, but,

* *v.* also Chap. xi., where the practice at the Broken Hill Block 14 Works, Port Adelaide, is described in some detail.

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generally speaking, it may be stated that the drawbacks to their use are—First, that their coking in the upper part of the smelting zone absorbs heat just where it is most wanted, while tending to heat the charge near the top, which should be kept cool. Second, that the sudden changes in volume, due to the progress of the carbonisation (especially of wood), and the increase in the quantity of gases given off, tend to increase the volatilisation of lead, and generally to cause irregularities in the furnace working.

Coke and Charcoal.—Comparing **coke** with **charcoal** it is to be noted that, on account of the tendency of all lead compounds to sinter together at a low temperature, comparatively little reduction can be effected by CO, and actual contact of molten drops of oxides and silicates with masses of glowing fuel has principally to be depended upon. Since CO, therefore, plays but a small part in the economy of the furnace, the fuel should be burned before the tuyeres as far as possible to CO_2, so as to give out as much heat as possible just where it is most needed; at the same time, the portion of the charge *above* the smelting zone should be kept as cool as possible, so as to prevent the CO_2 from being reconverted into CO by taking up carbon according to the reaction $CO_2 + C = 2CO$ with consequent waste of fuel and loss of heat.

Coke fulfils these conditions much better than charcoal, for, owing to its greater density and less porosity, much more CO_2 is produced in burning it before the tuyeres than is the case with the latter; while its higher igniting point renders it much easier to keep the smelting zone concentrated into a narrow belt and prevent the heat from rising (with consequent waste of fuel, increased volatilisation, decreased porosity of the charge, and other disadvantages which follow a rise of heat), which is so liable to occur when charcoal is exclusively used.

Another advantage possessed by coke over charcoal is its greater strength, which enables it to resist the weight of a much higher column of charge without crushing, and this is very important, especially when dealing with mixtures poor in lead and rich in iron requiring much lime flux, for it is impossible to properly smelt such mixtures except in a high furnace.

Charcoal labours under the disadvantage of breaking up in handling, and of crumbling or decrepitating in the furnace. Crushed charcoal is not only worthless as fuel, but makes unclean slags and increases the amount of flue dust. On the other hand, charcoal has less ash than coke, keeps the charge more open (on account of its greater bulk), and is more porous; hence weight for weight a fuel charge of mixed coke and charcoal will smelt more ore in a given time than one composed wholly of coke. The fuel consumption when using charcoal alone is, however, excessive, owing to the crushing which takes

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place, often reaching 30 to 40 per cent., so that a large proportion of coke is used when at all possible. Charcoal, moreover, deteriorates rapidly when stored, hence it is best used fresh.

The common practice among American lead smelters a few years ago was to use a mixture of coke and charcoal, by which, to some extent, the combined advantages of strength and porosity were realised, the coke supporting the charge, while the charcoal igniting first burnt away quickly leaving hollow spaces among the coke for the blast to penetrate. With modern high furnaces of ample size and slags rich in lime, however, there are many advantages (besides economy) in using coke exclusively, as, against a trifling decrease in furnace capacity and increase in quantity of slag formed, can be set the cleaner slags and smaller amount of flue dust. The coke used in Western America is very soft and ashy, the published analyses being no criterion of the latter point. Thus of cokes which are supposed to contain from 12 to 15 per cent. ash, like most of those from Southern Colorado and New Mexico, the author has frequently found trucks with as much as 21 to 23 per cent. ash, and has had whole train loads averaging 19½ per cent. This has to be considered in the consumption.

Anthracite of goose-egg size has been substituted by Ropp* for part of the coke charge of a furnace, with the result that when 60 per cent. of the coke was so replaced the furnace capacity was reduced by one-third, the working remaining normal in other respects, the furnace top being cool and the crucible hot, while the slags were clean and matte and speiss both low in lead. With charges containing 7½ per cent. zinc, smaller wall accretions seemed to be formed than when using coke alone.

Bituminous coal of assorted sizes from pea to lump has been used by Neill† to replace charcoal and part of the coke in a mixed fuel charge of coke and charcoal. With 27 per cent. of bituminous coal the crucible kept more open, the lead and slag appeared hotter, the tuyeres brighter, and the slag was cleaner than when coke alone was used. The smoke was thicker, but there was no more flue dust on account of the furnace top being cooler. The charges settled more evenly, and fewer zinc accretions formed than with coke alone.

Bituminous coal was also employed successfully by Austin‡ at the *Germania* Works, Salt Lake City, for eighteen months, but was abandoned owing to the arsenical and coppery ores smelted, as it was found to increase the amount of "top crusts" formed on the lead. At these works the fuel charge of 14 per cent. coke and 2 per cent. charcoal, which cost $1.33 per ton of ore, could be replaced by 9 per cent. coke, 2 per cent. charcoal,

* *Trans. A.I.M.E.*, vol. xx., p. 171. † *Ibid.*, vol. xx., p. 165.
‡ *E. and M. J.*, Dec. 15, 1894.

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and 6 per cent. nut coal, costing $1.07 per ton of ore smelted. Austin notes that coal produces a very explosive mixture at the feed floor, and that it tends to make the charge denser, so increasing the danger of this explosive mixture coming back into the blast main. He says—(1) That coal can only be profitably used when the saving in price over coke is considerable; (2) that it should always be combined with charcoal to counteract its density; (3) that the total fuel charge should be from 1 to 2 per cent. more than with coke alone; (4) that the feeding should be even and carefully watched; and (5) that it should not be used with ores carrying much arsenic and copper.

Gaseous fuel has been tried in the blast furnace, and replaced successfully as much as 30 per cent. of the coke charge. The substitution could hardly be a success financially, and from what has been said about the comparative reducing effects of solid carbon and of CO or other gaseous reducing agent, it is obvious that the replacement of solid fuel could, under no circumstances, be carried much further in the blast furnace.

Amount of Fuel Required.—The quantity of fuel required per ton of ore smelted is least :—

1. With ores rich in lead and, therefore, producing less slag.
2. With ores having a fusible gangue and comparatively free from zinc, magnesia, and other refractory ingredients.
3. With coarse ore, which permits free penetration of the blast and quick running of the furnace.
4. At the level of the sea, where the quantity of blast required is less.
5. In summer when the blast, being already at a temperature, say, 30° to 50° above that of winter, the fuel required is fractionally less.
6. In dry weather generally, when there is least moisture to be evaporated from the fuel, ore, and fluxes.

It is, of course, greatest under diametrically opposite conditions—*i.e.*, poor ores with refractory gangue in a fine condition, smelted at high altitudes in wet weather. The variations are in practice with coke from 12 to 22 per cent., with charcoal 20 to 28 per cent., and, in exceptional cases, even over 30 per cent.

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CHAPTER VIII.

BLAST FURNACE LEAD SMELTING—PLANT.

General Arrangement.—The general arrangement of a smelting plant, though perhaps more a question of engineering than of metallurgy pure and simple, is very important; for modern metallurgy is becoming more and more a question of engineering and less of empirical rule of thumb. A blast furnace plant always requires three levels—viz., those of the ore-delivery floor, feed floor, and slag dump. Where the site permits, there should be at least 8 feet between the first and second, and at least 16 feet each below the other two. In default of natural fall, however, elevators or hoists may be used for the feed floor, and in that case only sufficient fall is required to get in ore bins above the feed floor and to get away the slag at the dump level. The remaining details of arrangement will depend upon the site

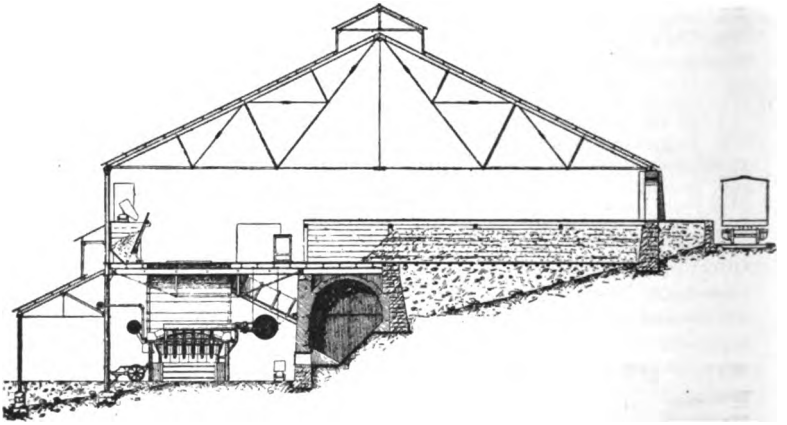

Fig. 51.—Common Arrangement of Smelting Furnace.

available, the railroad communications, the composition of the ores to be treated, and the regularity, or otherwise, of their supply; they vary so much that only practical experience can give the student some insight into the question.* A common

* For further information the student may be referred to Locke, *Smelting Plants*, Cincinnati, 1883; and to Hofman, *Metallurgy of Lead*, pp. 168 to 175. Detailed descriptions of existing smelting plants are also given in papers by the author and J. W. Malcolmson in *Proc. Inst. Civ. Eng.*, vol. cxiv., part ii.

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arrangement of furnace with dust chamber and feed floors is shown in Fig. 51.

General Consideration of Details.—Lead smelting blast furnaces were formerly built of brick or stone throughout, rectangular in section, blown by tuyeres in the back wall of the furnace only, and provided with an interior crucible or sump which was tapped at intervals into a "tap-pit" in front of the furnace. They were commonly made wider at the tuyere level than above, and may be seen figured in any of the older works on the metallurgy of lead. Their great disadvantages were—(1) *Low temperature in the smelting zone*, causing incomplete reduction of lead and separation from slag and matte. (2) *Comparatively high velocity of the effluent gases*, which caused a high temperature at the mouth of the furnace, an excessive consumption of fuel, and a very high loss of lead by volatilisation. (3) *Small capacity* with its inevitable concomitants, high cost of treatment, and great irregularity in working. (4) *Inaccessibility* of the interior and *want of control* over the furnace working except by blowing out. These furnaces are now quite extinct, having been replaced everywhere by higher furnaces, circular or oblong in section, having their walls protected by exterior iron casings and provided with tuyeres arranged symmetrically round the exterior instead of only at the back. The area at the tuyeres is kept constant either by the use of water tuyeres (Harz) or water blocks (Przibram), or, more commonly, by water-jacketing the whole smelting zone of the furnace. The two former systems are still in use to a limited extent in parts of Europe, but the latter have so many advantages that their use is to be recommended in every case where sufficient supply of water is obtainable at a reasonable cost. Where water is very scarce and refractory material easily obtained, there is much to be said in favour of the water-block and water-tuyere system, especially when the supply of ore is irregular.

The **tuyere area** in modern furnaces is almost invariably considerably less than the throat area, which is advantageous in two ways :—(*a*) because, by keeping the tuyere area small, the temperature of the smelting zone is high, a condition conducive to good reduction of lead and production of clean slags; and (*b*) because the widening towards the feed floor causes a diminished velocity in the ascending current of furnace gases, which promotes the absorption of the heat they contain by the cold charges, and greatly reduces the amount of lead carried off as flue dust and fume. As a rule, with circular furnaces the diameter increases gradually from the tuyeres to the throat, while rectangular furnaces are built with a bosh, which is preferable on account of the clearer definition of the smelting zone which it secures. In either case the area at the throat should be from two to two and a-half times that at the tuyeres, in order to

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ensure that the velocity of the gases shall be sufficiently slackened.

Lead furnaces may be charged either from the feed floor level, the fumes being removed by a downtake flue below the floor, or by means of charging doors in a chimney, or hood of brick, or sheet iron forming a continuation of the stack, in which case the gases and flue dust are taken off by an overhead downtake. Both arrangements are employed for oblong as well as for circular furnaces, but the former is more common.

The **height** of modern furnaces varies chiefly with the nature of the ores to be smelted. Ores rich in lead and producing a ferruginous slag are comparatively easy to smelt at a low temperature, which can be obtained with a low pressure of blast, and, consequently, a moderate height of 10 to 14 feet above tuyeres is sufficient. Ores poor in lead and rich in silica, to which a large quantity of limestone has to be added in order to form a calcareous slag, require, on the other hand, a high temperature and long continued heat in the smelting zone, only obtained by the use of a high pressure blast; consequently, a greater height of from 16 to 20 feet is required in order to prevent heat from being wasted at the surface of the charge.

The **number of tuyeres**, formerly from one to three, has been increased both in circular and in oblong furnaces to from eight to fourteen, according to the size of the furnace. The smallest number now employed in practice is five (Clausthal), but whatever the number, they are evenly distributed round the furnace. The diameter of tuyeres varies between $2\frac{1}{2}$ inches and 4 inches, but 3 inches to $3\frac{1}{2}$ inches are the sizes most commonly employed.

The **distance across the furnace** between the tuyeres varies in circular furnaces from 36 inches to 60 inches, but in oblong furnaces only from 32 inches to 42 inches. Increasing the size of circular furnaces, of course, results in greater capacity, but by no means in proportion to the increased area, while the pressure of blast has to be augmented in order to ensure penetration to the centre of the charge. The augmented blast-pressure requires, in order to preserve the reducing action, simultaneous increase in the height of the furnace, and is accompanied by the disadvantages of increased loss by volatilisation, and of a creeping upward of the smelting zone which reduces the temperature at the tuyeres. With circular furnaces of moderate height, moreover, the fuel has to be thrown towards the centre in order to allow the blast to penetrate and prevent the formation of a chimney of unmelted charge, while with oblong furnaces fuel, ore, and fluxes may be spread in even layers, which gives better reduction. The capacity of an oblong furnace may be doubled by simply doubling its length without interfering with its breadth or altering any other condition, whereas doubling the sectional area of a circular furnace does not result in doubling its

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capacity, unless the height and the blast pressure are increased proportionately at the same time.

For basic ores rich in lead and poor in silver producing fusible ferruginous slags, where the high volatilisation loss is comparatively unimportant, large circular furnaces may be employed with advantage (*e.g.*, Spain); but with ores poor in lead and rich in silver, and especially in cases where the slags produced are high in silica and lime, the oblong form is far preferable (United States, Mexico, Australia). The blast pressure employed with circular furnaces varies according to the height of the furnace from $\frac{3}{4}$ inch to $1\frac{1}{2}$ inches of quicksilver (6 to 12 ozs. per square inch) with a diameter of 36 inches to 42 inches. With larger circular furnaces of from 48 inches to 60 inches diameter the blast pressure must be increased to 2 inches (= 1 lb. per square inch) and even to $2\frac{1}{2}$ inches or 3 inches (= 20 ozs. to 24 ozs.), if the ores are at all infusible.

Lead furnaces may be provided with an interior "sump," which is tapped at intervals into an exterior "tapping box," or they may have an interior "well" or "crucible," which is always kept full of lead, and which communicates by means of a channel called the "syphon tap" with an iron pot, from which the lead can be ladled almost continuously. The former is the old arrangement still used in a few German lead furnaces, but now almost everywhere obsolete; the latter arrangement being in almost universal use. One great disadvantage of the sump furnace is that the operation of tapping interferes with the regular working of the furnace, a large mass of unsmelted material being suddenly lowered through the smelting zone, and the sudden contact of solid material with the bottom of the hearth, when the bath of lead is removed by tapping, is liable to give rise to the formation of "sows" and "bottom crusts," especially as during the tapping operation the blast has to be turned off for a while. Crusts will occasionally form on top of the lead in a crucible furnace but they are much more easily removed (by taking down a jacket) than in the case of those formed in a sump furnace.

The syphon tap for continuous discharge of lead from the crucible is an improvement of a very old form of exterior forehearth described and figured by Karsten; it was invented by a Clausthal metallurgist called Arents, and was first tried in Nevada, from whence it spread to every lead smelting district in the world. It is shown in Fig. 60, which represents an American circular water-jacket furnace; it consists simply of a tube built in the firebrick wall of the crucible and connected at the top with a basin-shaped depression in the same, which is sometimes provided with a cast-iron casing and is called the "lead well." Owing to the pressure on the lead in the crucible caused by the weight of slag and charge floating on it, the level

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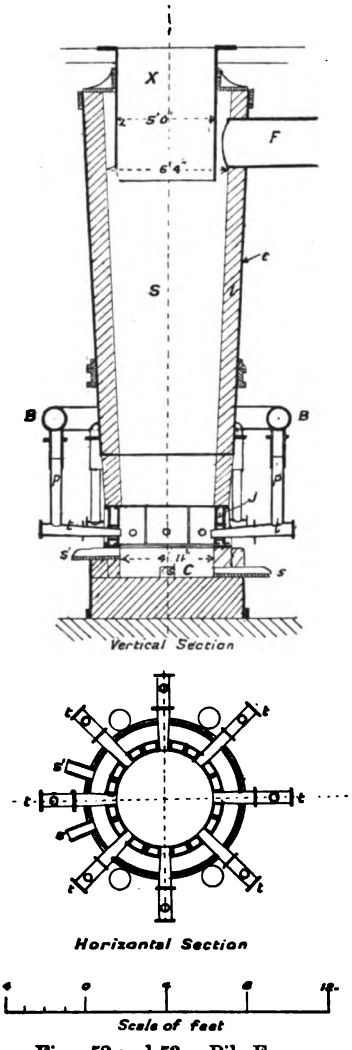
of the lead in the well is always some inches above that of the inside of the crucible, and with charges poor in lead there is some tendency to chill in the tube, which is guarded against by inserting in it from time to time red-hot iron bars. Besides the greater regularity in furnace working and the avoidance of "sows," the use of the "automatic tap" results in a smaller production of dross. It is, however, not to be recommended in the case of very coppery charges (as, for example, in concentrating lead matte containing upwards of 12 per cent. Cu), on account of the great tendency to form a "bottom crust" consisting of an alloy of copper and lead with a high melting point, which gradually grows up from the bottom till it fills the crucible. In these cases, therefore, it is better to abandon the automatic tap and work the furnace as a sump furnace, tapping from the bottom. Sump furnaces are also preferable in cases where ores have to be smelted which are exceptionally rich in zinc and in barium sulphate, like those of Goslar, which could not well be smelted in the ordinary way with an automatic tap, on account of the quantity of crusts which would form above the lead. By tapping from the bottom the hearth can be cleaned up at each tapping and the accretions removed.



Figs. 52 and 53.—Pilz Furnace.

The blast used in lead furnaces is almost always produced by a "positive blower" with rolling impellers of the Root type. The so-called "Baker" was formerly largely used in America, but those of the Root type are decidedly the best, be-

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cause they are made more strongly, and because of the much greater margin of speed permissible in running them; taking a Root and a Baker of approximately the same capacity at ordinary speeds and low pressure, the former can, in case of emergency, be worked up to more than double its proper speed without injury and without much loss of efficiency, whereas the efficiency of the Baker at high speeds and with pressures exceeding 1 lb. per square inch is very low.

Hot blast as yet finds no use in lead blast furnaces, for the temperatures required are only such as can be economically produced by burning fuel before the tuyeres with cold air. It is generally supposed that the use of hot blast would so increase the reducing effect of the furnace as to give rise to the formation of iron "sows" in the crucible, besides enormously increasing the loss of lead by volatilisation.

It may be convenient to consider first the circular furnaces, which are still commonly employed in Europe, and then to describe in greater detail the large oblong furnaces which are preferred in the United States, Mexico, and Australia.

CIRCULAR FURNACES.

The following types may be figured and described :—

1. The **Freiberg Pilzofen** with water jacket in sections, the prototype of all water-jacketed lead furnaces.
2. The **Lower Harz** furnace with simple water tuyeres.
3. The **Clausthal** furnace with water tuyeres and air-cooled boxes.
4. The **Przibram** furnace with water tuyeres and water blocks.
5. The **American** round furnace with water jacket in one piece and overhead downtake.

Of these, the first three are sump furnaces, while the two latter are provided with automatic discharge.

1. **The Pilz furnace**, invented at Freiberg by Bergrath Pilz, in 1863, is undoubtedly the first complete water-jacketed furnace ever used for smelting lead ores, and the prototype of the American water jackets. It is equally certain that at Freiberg, under Government control, the furnace has undergone but little improvement during the past twenty-five years or more, while in America it was very soon improved out of all recognition by a series of able German metallurgists, backed by powerful and progressive capitalists.

The water jacket of this furnace is of wrought iron, and is built up in segments, each segment having a tuyere aperture in the centre. The construction of the furnace is shown in Figs. 52 and 53. S is the shaft, *c* the casing of boiler plate surrounding the brick lining, *l*, which rests on four cast-iron columns. J are sections of the jackets, each 8 inches wide and 20 inches high, with an iron tube through which are inserted the tuyere

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nozzles, *t*. Cold water enters through a small pipe opening into the bottom of each section, while the hot water is discharged through another pipe at the top. The tuyeres are supplied with air by means of the sheet-iron bustle pipes, *p*, hanging from the cast-iron blast pipe, B, which surrounds the furnace. C is the crucible, lined with firebrick and furnished with two spouts, *s*, at the level of the bottom, for tapping lead and matte into the movable tapping box on wheels, and with others, s^1, at a higher level for the slag. F is the flue for the escaping furnace gases, connected with the general dust chamber and flue system of the establishment; X is the charging cylinder hanging in the centre of the throat. The capacity of the furnace, with a pressure of $\frac{1}{8}$ to 1 inch of mercury, is from 30

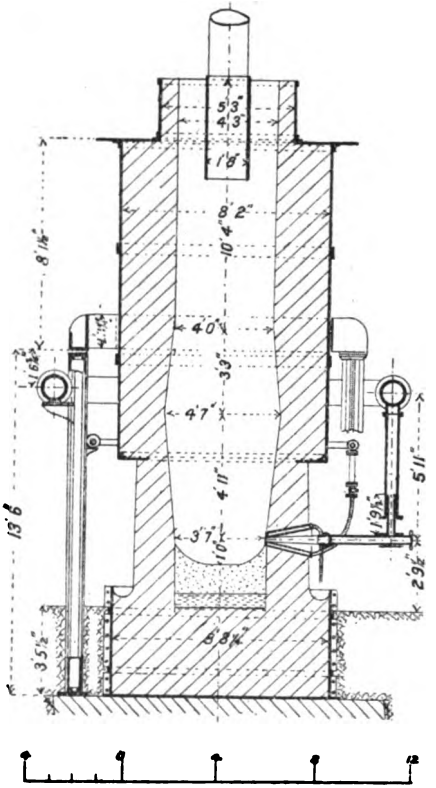

Fig. 54.—Lower Harz Furnace.

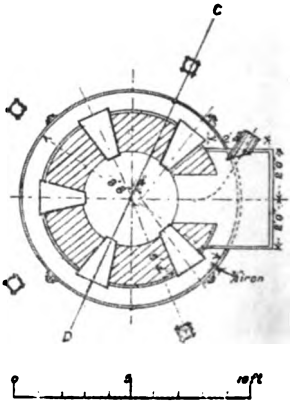

Fig. 55.—Section of lower Harz Furnace.

to 35 tons of ore per day, the coke consumption being 22 per cent. of the weight of ore. For further particulars of the furnace work *v.* Chap. xi.

2. **The Lower Harz Furnace.**—Of all the furnaces at work upon lead ores, this is, in some respects, the most primitive. Its construction will be seen from the vertical section, Fig. 54, and the horizontal section through tuyeres, Fig. 55. The sump

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is formed of "steep" (brasque) rammed inside the brick foundation, which is enclosed in iron plates to prevent leakage of lead. The upper portion of the furnace lining, above the smelting zone, wears very little, and is entirely supported on iron plates, forming a continuation of the outer casing, the whole of which rests on the four columns shown in the plan. The lining in the smelting zone, which wears out very fast, is thus easily repaired without interfering with the upper portion of the furnace. The height from tuyeres to throat is 18 feet 6 inches, and the tuyere level is 1 foot above the bottom of the hearth. The shaft is contracted immediately above the bosh in order to prevent, as far as possible, the formation of zinc accretions, by accelerating the speed of the ascending current of furnace gases and zinc fumes. The gases are drawn off by a tube of comparatively small diameter, suspended in the centre of the shaft, the advantage of which is that the current of gases is thus attracted towards the centre and away from the sides, where it is liable to deposit zinc accretions.

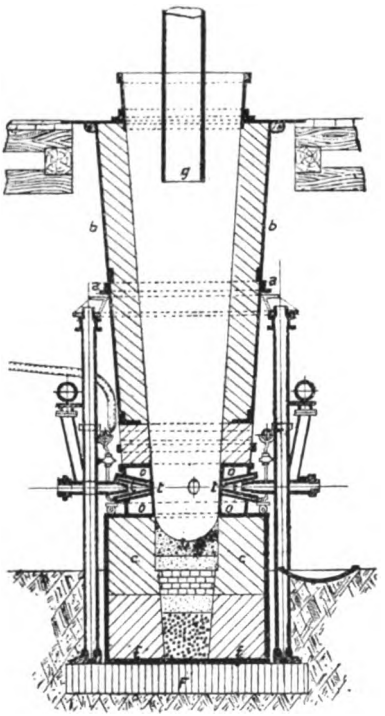

Fig. 56.—Clausthal Furnace.

The water tuyeres shown in the figures are inclined at an angle of 3°, and are 2 inches diameter; they are five in number, and disposed symmetrically round the perimeter of the furnace, as shown in the plan. The blast pressure is about $1\frac{1}{4}$ to $1\frac{3}{8}$ inches of mercury, and each furnace treats $8\frac{1}{2}$ to 10 tons of ore per day (*v.* Chap. xi.).

3. **The Clausthal furnace** is somewhat similar to the above in construction, but different in form. Instead of a bosh, it gradually increases in diameter from tuyeres to throat (Fig. 56). The whole furnace is built upon a stone foundation block, F, which supports a cast-iron foundation plate; the crucible is built of firebrick, enclosed by cast-iron plates, and encloses a succession of hearth layers, the uppermost of which is of

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brasque. The lining of the shaft is firebrick surrounded by a casing, *b*, of boiler-plate, to which are rivetted angle irons, *a*, by means of which the shaft is supported on hollow columns resting in cast-iron sockets, as shown. The furnace gases are drawn off through the tube *g*; the furnace has 4 water tuyeres, *t*, each 2½ inches diameter, supplied with air at 6 to 8 ozs. pressure. These water tuyeres pass through cast-iron cooling boxes, O, which are cooled, partly by a current of air and partly by the

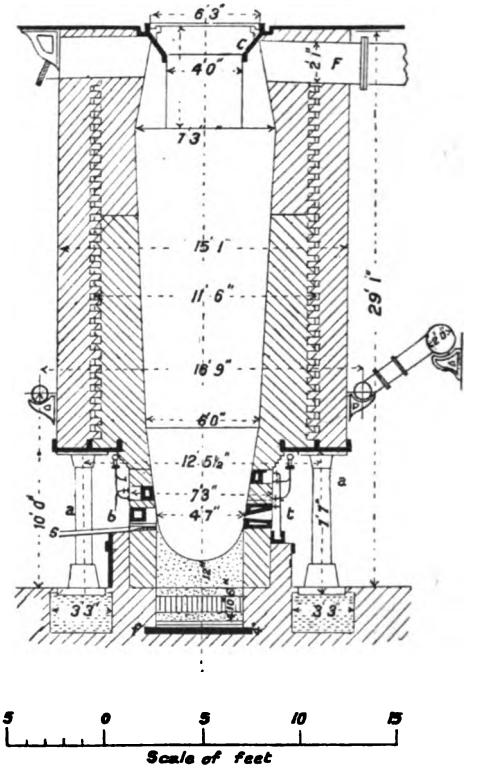

Fig. 57.—Przibram Furnace.

circulation of water in the water tuyeres. This seems a very imperfect arrangement, and the use of complete water jackets is certainly preferable; the practice in these furnaces of the "precipitation" process, elsewhere obsolete, is also peculiar, and will be described in Chap. xi.

4. **The Przibram Furnace.**—This furnace, shown in section in Fig. 56, is built somewhat after the pattern of an iron blast

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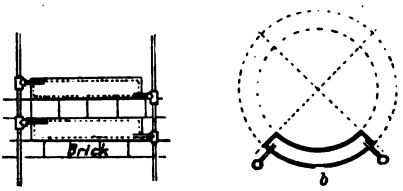
furnace in miniature. The walls are thick and double, with an expansion space between the inner firebrick lining and the outer wall of common brick; there is no exterior iron casing. The upper part of the furnace rests upon a framework of flanged cast-iron plates supported by six cast-iron columns, *a*; the smelting zone of firebrick is protected by three rows of cast-iron water blocks. The lower row contains eight water tuyeres, which are simply cast-iron boxes with a conical bushing cast through the centre, into which fit the sheet-iron tuyere nozzles. The water block over the slag spout, *s*, is of a peculiar shape. The two upper rows are composed of larger "water blocks," *b*, of cast iron (Fig. 59) alternating with brick, as shown in Figs. 57 and 58. The crucible of the furnace is composed of layers of rammed "brasque" on a layer of brick, under which again are other layers of sand and loam, the whole being supported on a massive cast-iron foundation plate, *f* (Fig. 57), to avoid leakage of lead. The discharge of lead from the crucible takes place automatically by means of Arents' syphon tap (not shown in the figure) as in American furnaces. Charging is performed by means of a cast-iron cup, *c*, with sheet-iron curtain hanging from it, the furnace gases being taken away by the flue, F, below the charging floor



Figs. 58 and 59.—Przibram Furnace—Water Blocks and Bricks.

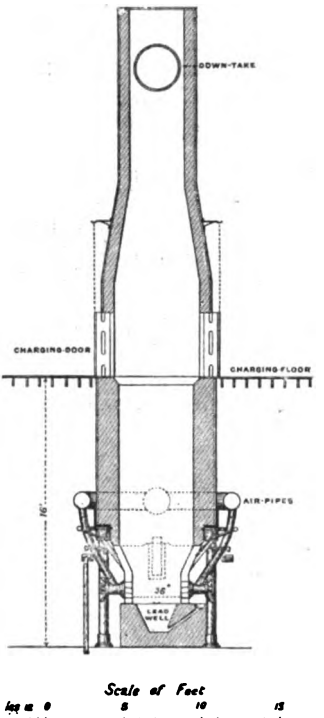


Fig. 60.—American Circular Water Jacket Furnace.

One of these furnaces with 2½-inch tuyeres supplied with air at a pressure of 1·6 inches of mercury smelts in twenty-four hours 31 tons of charge (= 22 tons of ore), with a coke consumption of 16·4 per cent. and about ¾ per cent. charcoal (1½ bushels

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per ton). Further details as to the working of the furnace are to be found in Chap. xi.

5. **The American Circular Water Jacket.**—One variety of this furnace is shown in sectional elevation in Fig. 60, in which the charging floor and doors are plainly visible, as are also the blast pipes, tuyeres, and the outside lead well communicating by means of the automatic tap with the interior crucible. The whole shaft of the furnace is cased with iron plates, a continuation of which forms the stack, and the iron casing and stack, together with its lining, is supported on four heavy cast-iron columns. This particular furnace is fitted with the Devereux patent tuyeres, to be described in their place, and is charged from both sides, the flue dust and waste gases being removed by an overhead downtake.

Circular furnaces were used at Eureka, Nevada, and, in the early days of water-jacket smelting, all over the U.S. At *Mine La Motte* and other places in Missouri, furnaces more or less of this type are still in use. The diameter at the tuyeres is from 3 feet 9 inches to 4 feet 3 inches, the jackets are 3 feet 6 inches high, with a bosh of 3 inches, which is continued upwards to the charging floor 8 feet to 10 feet 6 inches above tuyere level. The crucible is 2 feet 6 inches deep, provided with automatic syphon tap for the lead, and the brick stack above the water jackets has a boiler-plate casing, and is supported on columns in the usual way. There are five or six tuyeres supplied with air at a pressure of 1 to 1½ inches mercury.

Circular water jackets are in use at Coueron* and Pontgibaud† (France), at Mazzaron ‡ and Puertollano§ (Spain), and at many places in Mexico and other countries. They are most suitable where labour is cheap and the ores not too siliceous. With large supplies of siliceous or refractory ores, poor in lead, they give way to the large oblong furnaces.

RECTANGULAR FURNACES.

The original oblong furnaces were of the Raschette type, first employed in the Urals for iron smelting, and subsequently in the Upper Harz for lead-silver smelting. These furnaces were not water-cooled; they were 16 feet 3 inches from tuyere level to throat, and measured 3 feet by 6 feet 6 inches at the tuyeres. On each long side were situated five 2-inch tuyeres; the hearth was saddle shaped, so that at each end there was a sump made of brasque which was tapped at intervals into an outside tap-pit in order to facilitate separation of the melted products. The modern American water-jacketed furnace presents but few points of resemblance with its humble prototype.

* Phillips, *Elements of Metallurgy*. † *Ibid.*
‡ Sanchez y Massia, *Metallurgia del Plomo*, Madrid, 1893. § *Ibid.*

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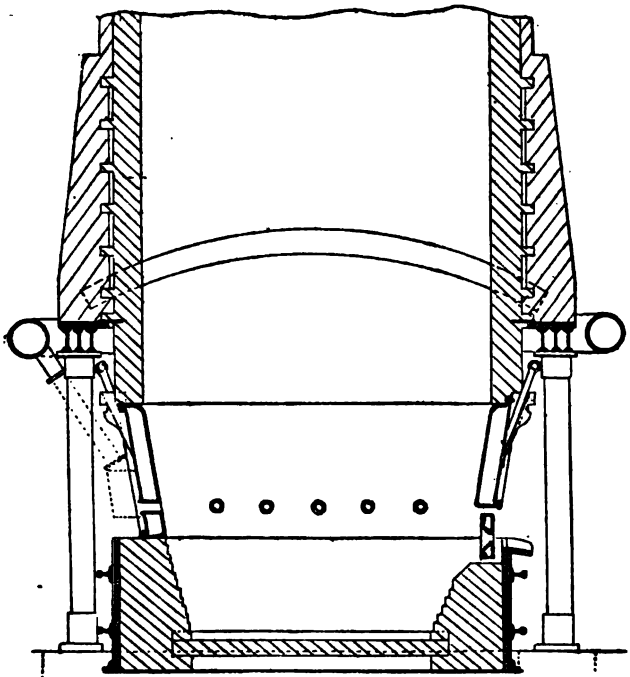

Fig. 61.—Rectangular Furnace—Sectional Elevation.

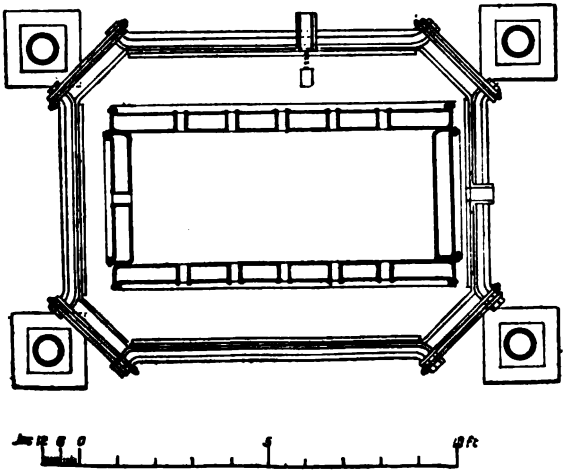

Fig. 62.—Rectangular Furnace—Sectional Plan.

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Two principal modifications of furnace may be described according as the jackets are of cast- or of wrought-iron, the dimensions and other details of construction not necessarily differing in the two cases. Figs. 61, 62 and 63 * show a furnace

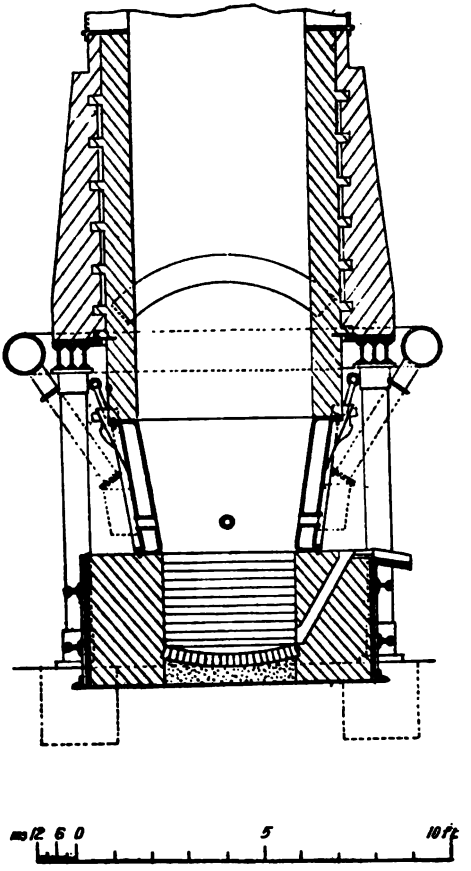

Fig. 63.—Rectangular Furnace.

with wrought jackets erected at Great Falls, Montana, in 1891. Fig. 64 shows the lower part of the most recently erected furnace at the Globe Smelting Works, Denver, 1895; while Figs. 65 and 66 show the new furnaces of the Broken Hill Proprietary Block 14 Company at Port Adelaide, South Australia (1897).

* Borrowed from Hofman, *Metallurgy of Lead*, 1892.

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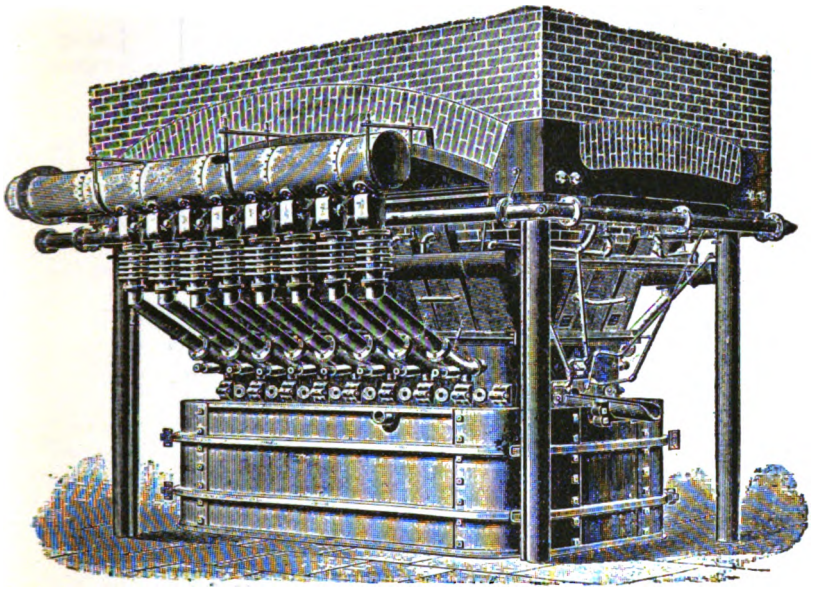

A RECENT SILVER-LEAD FURNACE

Fig. 64.

Dimensions.—The sectional area of modern oblong furnaces has been increased during the past fifteen years by increasing the length, it being, as already pointed out, impracticable to widen these furnaces without serious disadvantage. Fifteen years ago or so, there were few furnaces in existence over 6 feet long, whereas nowadays 120 inches to 140 inches is the usual size, and some have been built even 160 inches or over 13 feet long. The width at tuyere level varies between 2 feet 6 inches and 3 feet 6 inches; a few years ago the tendency was to reduce the width to 30 or 33 inches in order to use a lower blast pressure and prevent the heat from creeping up, but of late most of the new furnaces erected are 40 or 42 inches across tuyeres, corresponding with the increase in height and with the increased rapidity of driving.

As already mentioned, the height of water-jacket furnaces has been increased of late years to cope with the more refractory ores now smelted and the more infusible slags produced, the most recent furnaces — except those working on zinciferous ores with very ferruginous slags—being generally 17 feet to 20 feet from tuyere level to stock line.

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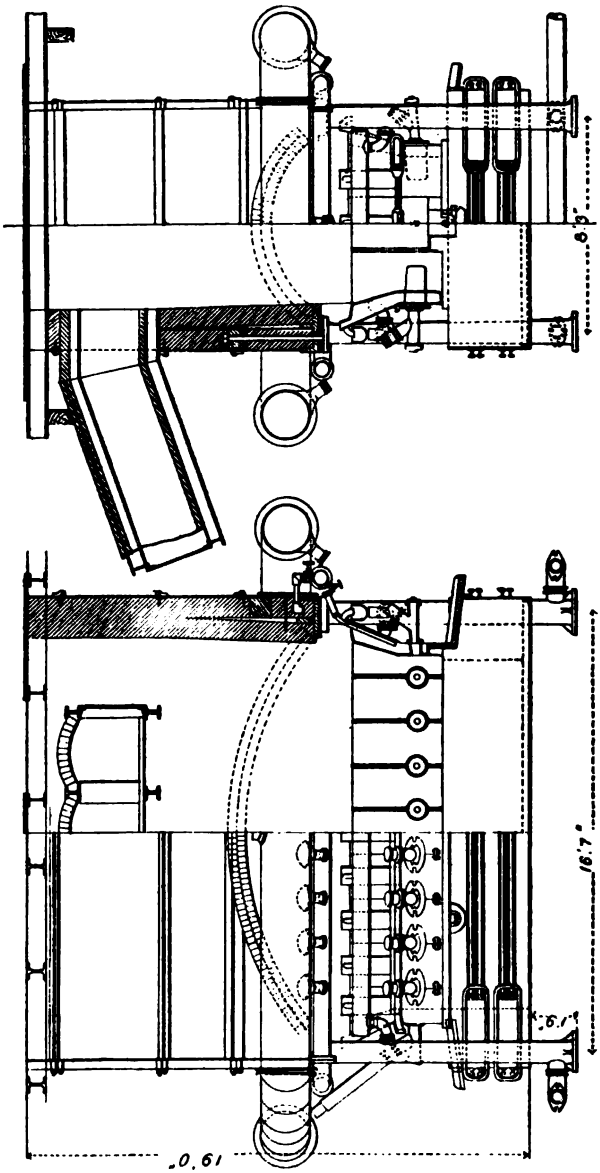

Fig. 65.—Arrangements for Charging Furnace.

Fig. 66.—Arrangements for Charging Furnace.

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1. **Foundation.**—A good foundation is essential, and solid rock is always best, unless more than 10 feet from surface, in which case a frame work of heavy planking placed crosswise and embedded in concrete may serve instead. The excavation should be at least 3 feet larger each way than the furnace bed plate, and is filled either with good rubble masonry, brick work, or a block of concrete into which are rammed as many large stones as possible, cement being in any case mixed with the mortar. The best of all possible foundations is formed by filling the excavation with molten slag, forming, when cold, a single block; but this is only attainable for additions to plant in an already existing works where a sufficiently quick succession of slag pots can be obtained. In any case, the topmost course must be perfectly smooth and level which, in a new works, is secured by making it of brick, and when molten slag is available can be easily obtained by forming shallow dams with pieces of bar iron (the tops of which are carefully levelled) and then filling them successively with molten slag. When a perfectly even and level foundation has been obtained, a layer of clay mortar is spread over it, and then the wrought-iron or steel "base plate," $\frac{1}{4}$ inch or $\frac{3}{8}$ inch thick is laid in position. This plate has generally a rim of $1\frac{1}{2}$-inch angle-iron rivetted on to assist in holding the hearth castings or "caisson plates" in position, and its function is to prevent leakage of lead from the well or crucible.

2. **Crucible with Automatic Tap.**—The crucible of this furnace, built up on the bed plate, of firebrick laid as closely as possible with thin fireclay mortar, is surrounded by thick "crucible castings" or caisson plates, which have to be very strong in order to resist the pressure of the lead in the crucible, frequently 20 to 25 tons dead weight of lead alone, without counting the downward pressure of the column of charge which floats upon it. These castings are commonly strengthened with projecting ribs, and bolted together. Their great weight, however, renders them very awkward for use in localities remote from railroad facilities, and at many modern works in America, as well as in the various Australian plants, they have been done away with, being replaced by bent rails enclosing a boiler plate outer casing, as shown in Figs. 61 and 62. Hofman indeed suggests* that the outer casing of the crucible should be oval in form, when it could be enclosed in a rivetted boiler plate shell strengthened by means of continuous bands of flat bar iron, but, though a very practical suggestion, the author is not aware that it has ever been put into practice.

Inside the plates the well is built up, a space about 2 inches wide being left between them and the firebrick, which is afterwards tamped with sand or brasque, so as to allow for expansion. The Arents automatic tap is simply an inclined channel half-

* *Op. cit.*, p. 186.

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a-brick wide, which is left from the bottom of the crucible—generally at the centre of one side—to the outside, where a basin is formed called the "lead well." Formerly this was formed by a semi-circular casting bolted to the crucible castings, but it is now wholly enclosed by the latter, and either a spout or a taphole is provided for the lead to flow into a cooling pot, which may be either fixed or, more generally, run on wheels. In some old furnaces a lead well on each side was provided, but, except in the case of large furnaces running on very rich lead ores, this is simply a waste of heat, and in most modern furnaces only one is seen. Two slag spouts are, however, frequently found, one at each end of the furnace, as with the help of a spout at the back which can be used occasionally or on alternate shifts, when the side instead of the end of the furnace is presented to the dump, crusts can frequently be prevented from forming.

3. **Shaft.**—At each corner of the foundation stands a column (usually of hollow cast-iron) about 8 inches diameter and 1 inch thickness of metal with capital and base, each 16 to 20 inches square and 2 inches thick. Upon these columns is set the "deck frame," which supports the whole of the furnace walls with their lining. In old furnaces this was composed simply of cast-iron plates 1½ to 2 inches thick, with strengthening flanges 3 to 9 inches deep, part of the direct pressure being taken off by arches in the brickwork. These light plates, however, were always giving trouble by bending and breaking, owing to unequal expansion, and in all modern furnaces the deck frame is composed of three T beams supporting a plain flangeless cast-iron deck plate, as shown in the Figs. 61 and 63. The T beams are bolted firmly to each other and to the capitals of the columns, the cast-iron plates simply resting on the former, so that there is no lateral thrust on them caused by unequal expansion. The lateral thrust of the brick arches was formerly taken up by the tie-rods only, but now strong flanges at the corners of the deck frames assist in taking it, as shown in Fig. 64. In some of the most modern furnaces arch beams are introduced to support the heavy furnace walls, as shown in Fig. 64.

The furnace walls resting on the deck plates are usually of common brick with an inner lining of firebrick, an expansion space being left between the two layers. In places, however, where firebricks are obtainable at not more than double or two and a-half times the cost of common brick, it is true economy to build the stack of firebricks throughout, their greater strength giving practical immunity from repairs. The walls of all modern furnaces are made much thicker at the bottom than the top, to diminish the loss of heat by radiation.

The whole shaft is well braced with tie-rods and corner-irons, which are usually cast-iron "brick stays" with heavy lugs to receive the tie-rods, as shown in Fig. 65.

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In some recent furnaces, and notably in those designed for the "British Broken Hill Company," the whole upper part of the furnace shaft is made of wrought-iron and mild steel water jackets, as has been done with copper furnaces for many years past. This was expected to facilitate the "barring down" of zinc "hangings," and to give an indestructible shaft. In practice, however, these long side sections have been found to give considerable trouble by buckling, and their cooling effect is so great that there is a quite perceptible increase in the fuel consumption. The zinc hangings do not seem to separate so easily from the smooth iron surface as was expected, while the quantity of accretions which form is (owing no doubt to the powerful cooling effect) much greater than with the ordinary brick stack. The use of these upper jackets has not, therefore, been extended.

4. **Charging and Fume-collecting Arrangements.**—One arrangement is to have an overhead stack and downtake for the furnace gases, built either of brick or of sheet iron, the charging being done through doors in each long side. This style is used in the Arkansas Valley (Leadville), Germania (Salt Lake City), Colorado Sm. Co. (Pueblo), and Montana ditto (Great Falls) works; it answers very well for charges low in zinc, but is not so suitable where there is much zinc, and, consequently, much "barring down" to be done. The other and, perhaps, more common arrangement is to feed the furnace from an open top, drawing off the gases below the feed floor, as shown in Figs. 65 and 66; this system is preferred at the Philadelphia (Pueblo), Globe (Denver), and all the Australian works; it is much more convenient in some respects, but requires a greater height from the slag floor and a more powerful draught to prevent the fumes from escaping on to the feed floor.

The feed floor is made of cast-iron plates with planed edges spliced together by wrought-iron plates underneath and bolts with countersunk heads. In order to avoid the exit of fumes on to the feed floor when open tops are employed, the old device was to provide each furnace with a telescopic ventilating hood made of sheet iron, consisting of a fixed chimney in the roof with a hood and smaller pipe sliding up and down in the former, and counterbalanced with weights so as to be easily moved up and down. These hoods have now, in most cases, been abandoned. Another arrangement employed until recently at some large works (including the Grant works, Denver, and the El Paso works) is the Pfort curtain. This consists of an oblong or elliptical "thimble" of thick sheet-iron extending downwards from the charging floor as far as the level of the bottom of the "take off," and, at least, a couple of feet each way smaller than the furnace top. This concentrates the down draught into a smaller space, and is found to trap the fumes effectually, but

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has the great disadvantage of being very much in the way when wall accretions have to be barred down, and, therefore, has been of late very generally discarded, being especially inapplicable in works where high zinc charges have to be treated.

The best arrangement for open charging is to allow the cast-iron floor plates to nearly cover the mouth of the furnace, except two spaces each about 4 feet by 2 feet, which are sufficient to enable the feeder to spread the charge in any desired fashion and to reach any part of the walls with a bar. Under ordinary circumstances these charging holes are left uncovered, but when blowing out, a cast-iron plate is placed over each opening and luted down with clay or wet ore fines. The iron plates round these openings are not a permanent part of the feed floor, but are readily removable for barring down when required.

It is a matter of observation that furnaces with open tops require a much stronger chimney draught in order to prevent the escape of fumes on the feed floor than those which are run with closed top, and this extra draught usually means extra loss. Some modern furnaces, therefore, are provided with the old fixed sheet-iron stack and hood in the roof overhead, connection with which is ordinarily made by means of a sheet-iron casing, the size of the furnace area, running on wheels and provided with side charging doors similarly to closed-top furnaces. When required, this casing can be run back for barring down.

The German plan of taking off the fumes by means of a small iron pipe suspended in the centre, and the plan of charging by means of cup and cone, as in iron blast furnaces, have both been tried but have not found favour, chiefly on account of the difficulty of obtaining free access to the furnace shaft for barring, &c., with such devices. With closed tops, a single overhead sheet-iron downtake, 5 feet to 7 feet diameter, is the usual practice, and, with open tops, a rectangular brick-lined downtake at the back or in the centre of one side of the furnace is the invariable arrangement.

A good deal of sickness (lead colic) used to be caused on the feed floor, as well as below, by fumes rising from the slag tap and lead well. The danger of lead poisoning is found to be minimised by completely partitioning off the feed floor from the lower part of the building, and providing the lower floor with its own series of shaft ventilators of sufficient size over each slag tap or between each pair of furnaces, and extending clear through the feed floor above the roof. They take up but little room on the feed floor, and ventilate the lower floor very effectually.

5. **Water Jackets.** — These may be either of cast- or of wrought-iron (in modern practice the former are usually preferred), but in any case their usual height is from 3 to 4 feet, the centre of the tuyeres being 10 inches from the bottom and the "bosh" of 6 to 10 inches, commencing from 8 inches to a foot

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higher up, to be continued in the brickwork. It will be borne in mind that the jackets have no weight to support, except that of the three or four layers of brick between their upper surface and the "deck plates"; they need not, therefore, be very heavy; in fact, they stand best when made as light as possible. They are almost invariably made with a bosh, but at the *Aurora* Works (Chicago, Ills.), Eurich * still uses a straight jacket and inserts water tuyeres 12 inches into the furnace to narrow the fusion zone to the required extent, the advantages claimed being the greater facility of barring off accretions, and a small but noticeable saving of coke, owing to the fusion zone being kept at a greater distance from the jackets.

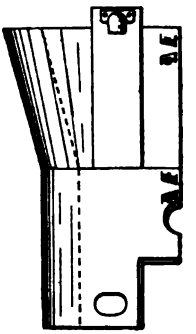

Fig. 67.—Cast-iron Water Jacket.

Cast-iron Jackets.—These are generally from 4½ to 6 inches inside measurement, the latter size being, perhaps, most common; and the iron is from ⅜ to ¼ inch thick, ⅝ inch being, perhaps, the commonest; frequently the inner skin is made double the thickness of the outer, as at Broken Hill. The water feed may be through a pipe screwed into the outer skin (Fig. 68), or through an open feeder forming part of the casting (Fig. 67); in either case, sufficient head must be employed to ensure the jacket being always full of water, which is secured by allowing the hot-water exit to rise some inches above the top of the jacket. The complete casing of a 120-inch furnace will be made up of sixteen sections, in twelve of which the side jackets are exactly alike, each having lugs with which to bolt it to its neighbours and a tuyere hole cast in the centre. The front and back breast-jackets are each in two pieces, right and left, and in a number of modern furnaces are unprovided with tuyeres. In some cases they are made curved and they never extend down to the top of the crucible, but stop some 10 inches above it, a common shape being that shown in Fig. 67, where the curved end-jackets extend right down at the sides, but leave an open space in the centre. The remaining space may be closed simply by pillars of firebrick with a clay slag tap in the middle, or by a tapping jacket, as is the more modern practice. The best arrangement is to have a tapping jacket 14 inches high, and to sink it 4 inches into the crucible wall, which helps to prevent leakage of lead from the front of the furnace, the actual slag tap being a conical hole in the jacket, only 2½ inches diameter on the outside, widening to 5 inches inside. In a small works, however, where the ore mixture varies widely in composition, especially if the ores be at

* *Priv. comm.*, 1896.

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all zinciferous, it is best to work with a firebrick breast instead of a tapping jacket, as it is then easier to get at crusts which form on top of the lead. Cast-iron jackets are now always supplied with handholes for cleaning, and the feed water has been, in one case at least, introduced through this handhole, which can, however, hardly be considered an improvement.

Detailed sections of cast-iron jackets are shown in Figs. 68* and 72,† the latter showing a novel arrangement for supporting each jacket separately and independently of the lugs which fasten it to its neighbours, the former being peculiar in its use of water tuyeres and in having a goose-neck iron pipe screwed into the top to serve as water discharge.

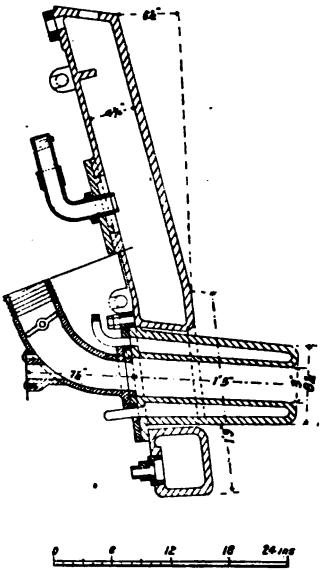

Fig. 68.—Section of Cast-iron Water Jacket.

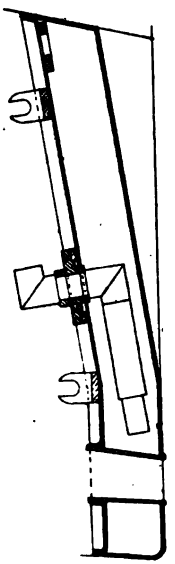

Fig. 69.—Section of Cast-iron Water Jacket.

Wrought-iron jackets are usually made of the same height as those of cast-iron, but only four sections are required—viz., one for each side and end. The old form of wrought-iron jacket had a feeder bolted on similar to that of the cast-iron jackets (Fig. 69); another form of wrought-iron jacket with feeder is that shown in Fig. 70, which, instead of a distinct bosh, slopes continuously from bottom to top. Another, and perhaps on the

* Beardsley, *Trans. A.I.M.E.*, vol. xxi.
† Broken Hill Prop. Coy., *Private notes*, 1896.

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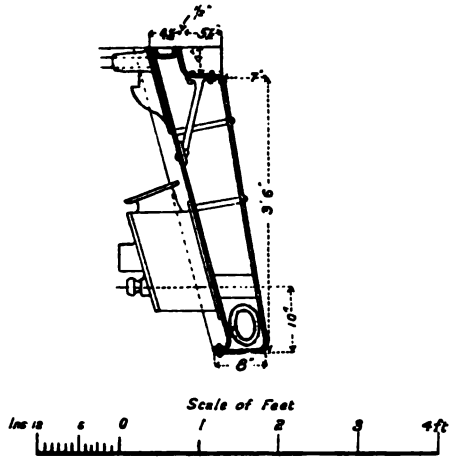

Fig. 70.—Section of Wrought-iron Water Jacket.

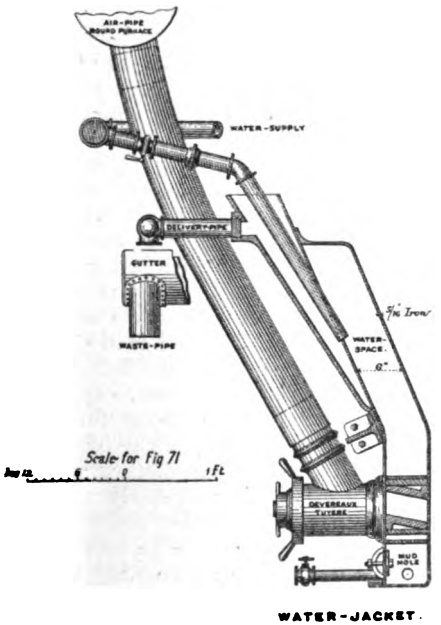

Fig. 71.—Section of Water Jacket.

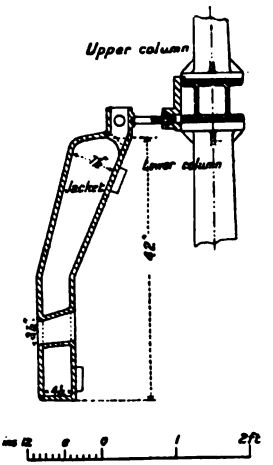

Fig. 72.—Section of Water Jacket.

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whole the best, form is that of the British Broken Hill furnaces, Fig. 69, which has wrought-iron pipes screwed in for both the feed water inlet and outlet. In any case, each section is provided with one or more handholes for cleaning out scale or sediment (*v.* Fig. 70), and the walls of the long side-sections at any rate are stiffened by stay bolts.

Terhune* highly recommends jackets of **cast steel**, which have been used since 1886 at the Hanauer Works (Salt Lake City). The sections are $\frac{5}{8}$ inch thick, tapped for two bushings $1\frac{1}{2}$ inches diameter for cleaning purposes, the same holes serving for water-feed and discharge by means of $\frac{3}{4}$-inch pipes in the plugs.

Comparing cast-iron with wrought-iron or mild steel, it should be noted that anywhere within reasonable distance of a foundry the former are cheaper; for not only do they last about as long when properly made, and cost less, but, when replaced, the value of the old metal is a considerable discount off the price of new jackets; whereas a discarded wrought-iron section is of no value as scrap. Cast-iron jackets are specially to be recommended where the water is very hard or very acid. Where, however, foundries are not accessible and the cost of carriage is high, the wrought-iron jackets frequently turn out to be cheaper in the long run, though the first cost may be higher.

The details of **water supply** are shown in Fig. 65; the cold water feed pipe surrounds the furnace under the blast pipe, each jacket has a branch of its own, by which the water enters at the top and sinks to the bottom as best it may, the hot water overflowing through a spout into a galvanised trough surrounding the furnace, and emptying itself into one or more stand pipes at the corners. The more modern way, however, is to replace these spouts and troughs by long pieces of gas pipe reaching to the stand pipes near the corner columns, which latter, indeed, are themselves frequently made to serve the functions of stand pipes (Fig. 65). In recent practice all the jackets are often connected at the bottom by short 1 inch nipples joined by thick rubber hose, so as to enable any one jacket to be fed from its neighbours in case of failure of its own proper water supply.

As to the **quantity of water required**, an ordinary furnace of 120 by 42 inches will take, in summer time, about 55 gallons per minute, supposing the water to be run into shallow ponds to be used over again while still warm, as is frequently the case. It is economical both as regards fuel consumption and wear and tear of jackets to keep the water supply to the jackets low, so that the escaping water shall be as hot as possible without generating steam.

It may be reckoned that in normal work a furnace with

* Hofman, *Metallurgy of Lead*, 1891.

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jackets 3 feet 6 inches high will require as a minimum from 1½ to 2 gallons per minute, according to the temperature of the water, for every foot of internal perimeter at the tuyere level, and double this amount must be allowed for blowing in or out. Furnaces with higher jackets will, of course, require more water, but not in proportion to the increased height.

6. **Blast.**—The blowers are usually of the Root pattern, with its modifications and improvements, the Baker blowers formerly so widely in use having been largely discarded for reasons already given. For a single furnace, 33 by 100 inches or upwards, one No. 6 Root blower is required, but there is considerable economy in running all the furnaces from a common blast main of ample dimensions, regulating the amount delivered to each by blast-gates on the several blast pipes. In a large works running several furnaces this arrangement is both simpler and cheaper than giving each its own blower, part of the blowing power calculated on the above liberal basis being then always in reserve. The blast main should be one-third greater in sectional area than the combined areas of the blower outlets Each branch blast pipe is tapped for a nipple, to which a pressure gauge is (or should be) affixed, the pressure being measured variously by columns of mercury, water, or glycerine. Two inches of mercury or 27 inches of water are equal to a pressure of 1 lb. per square inch.

Although the common blast main, with branch pipes, is so common and so convenient, attention may be called to the fact that it is impossible on this system to regulate the working of each individual furnace to such a nicety, especially when running on different charges, as by providing each furnace with its own blower. The latter system is advocated in Australia by Greenway (Port Adelaide), and in America by Eurich (Aurora), and on this principle the pressure gauge attached to each furnace becomes a delicate barometer, showing accurately the changes in the mechanical or physical condition of the column of charge above the tuyeres, which it never can be when utilised partially for the purpose of regulating the speed of the blowers or the number of individual blowers, delivering into a general blast main, which should be started or stopped.

Blast Pressures. — Not many years ago 20 to 24 ozs. per square inch were regarded as high pressures for the lead blast furnace; to-day, however, in the high furnaces of the most modern practice pressures of 2¼ to 3½ lbs. per square inch are commonly employed.

The comparatively low efficiency of all revolving blowers under these high pressures has led Iles * boldly to discard them altogether in favour of the overhead blowing engines, so familiar in connection with iron blast furnaces. The original cost is

* Globe Works, Denver, *Private notes*, 1897.

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considerable, but the efficiency and economy in working more than makes up for the interest in a large works.

7. **Tuyeres.**—The diameter of tuyeres varies from 2¾ inches in some small furnaces up to 3½ inches in those of the largest size. The ratio between the area of the tuyeres and the sectional area of the furnace at the tuyere level is a very important one, for upon it largely depends not only the capacity, but also the reducing effect of the furnace. The number of square inches of total tuyere area per square foot of effective sectional area between the tuyeres may be conveniently termed the "**tuyere ratio**" of the furnace. According to Hahn's rule one 3-inch tuyere is required for each square foot of sectional area at the tuyeres, which is equivalent to a tuyere ratio of 3·53—very closely adhered to up to a few years ago. Where slags high in lime and in silica have to be made, and a powerful reducing action is required, this ratio is somewhat reduced; thus the *Broken Hill Proprietary* furnaces, with an effective sectional area of 44 by 112 inches, have eleven 3½-inch tuyeres, which gives a tuyere ratio of 3·15. The tuyere ratio is still further reduced with the higher furnaces and blast pressures and more rapid driving now so common; thus the 45 by 140-inch furnaces of the *Germania* and *Pennsylvania* works at Salt Lake City have only fourteen tuyeres, 3 inches diameter, the tuyere ratio being only 2·19. When, on the other hand, a basic, zinciferous, and sulphurous charge has to be smelted and an oxidising action is aimed at, the tuyere ratio must be increased; thus at the *Block 14 Works*, Port Adelaide, the large furnaces (shown in Fig. 65), with effective area of 40 by 160 inches, have no less than eighteen tuyeres of 3½ inches diameter, giving a tuyere ratio of 3·90.

The tuyere nozzles are sometimes of bronze or brass (though now commonly of cast iron), bored and turned to fit as closely as possible into the conical holes in the jackets, which should be bored out to fit. In the ordinary form of tuyere the bronze nozzle is rivetted on to a galvanised or sheet-iron elbow, and connection is made to this from the nipples on the branch blast pipe, either by means of canvas bags soaked in alum or water glass, to render them incombustible and air tight, and tightly wired on, or, better, by means of close-fitting sheet-iron pipes. A peep hole at the back of the elbow is provided with a glass or mica eyepiece which can be removed when it is necessary to "rod" the tuyeres. The construction of the ordinary form of tuyere will be seen by reference to Fig. 73, which is, however, provided with the Davies slag escape shortly to be described, and in which *e* is the cast-iron elbow, *p* the peephole, and *n* the brass tuyere nozzle, the pipe with attachments between *e* and *n* being the slag escape, an ingenious contrivance devised to obviate the bad effects of slag overflowing into the tuyere pipes, a not uncommon accident due to carelessness of the tapper. It

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consists of a piece of 4-inch pipe, *a*, screwed into the cast-iron elbow and turned so as to fit neatly into the brass nozzle; on its under side is rivetted the flange, *b*, with lugs, *f*. These hold, by means of screws, *c*, the perforated sheet iron, *e*, against the perforation in the bottom of the pipe, the hole being closed by the diaphragm, *d*, which is merely a piece of cloth or thick paper. Should slag get into the tuyere pipe, it immediately burns a hole in the diaphragm and the blast escapes with a noise that attracts the attention of the furnace keeper. The screws, *c*, can be loosened in a moment so as to insert a new diaphragm.

The ordinary tuyeres employed are flush with the inside of the jackets, but the furnaces at *Aurora* (Ills.) and the whole of those at the various *Broken Hill* plants (Australia) are peculiar in having water tuyeres which extend into the furnace on both sides and so narrow the zone of fusion. At Aurora, the side

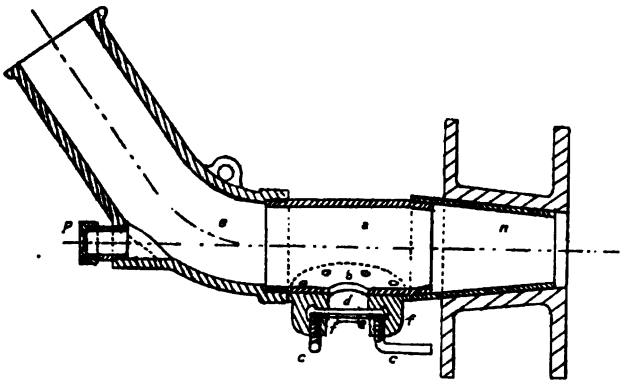

Fig. 73.—Tuyere.

jackets are straight (*i.e.*, have no bosh), and the tuyeres project 10 to 12 inches into the furnace; at Broken Hill, the side jackets have the usual bosh, and the tuyeres project inwards only 6 to 8 inches. The object in both cases is to decrease the amount of wall accretions and effect at the same time a trifling economy of fuel.

The ordinary tuyere pipe is subject to more or less leakage of air, and several forms of tuyere box have been introduced with the object of making a handy air-tight joint. One device, formerly in common use, is that of *Devereux*, shown in Figs. 60 and 71; it consists first of a bored and turned bronze tube fitting into the aperture in the jackets (which must be made specially large if this tuyere is to be used), and inside which an iron sleeve with a diagonal bore is fitted so that it can be revolved. The blast can, therefore, be turned in any direction (except the most

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generally useful—namely, centrally), which was supposed by its inventor to be a great advantage. The weight of the Devereux tuyere renders it very clumsy, and in the author's opinion the advantages of being able to alter the direction of the blast within such limits are at least problematical.

When, from any cause, the blast is stopped, unless the valves connecting the tuyere pipes with the blast pipe are immediately closed, combustible gases from the furnace travel back into the pipes, mix with the air, and may form an explosive mixture, which, taking fire from the tuyeres, may wreck the blast main and apparatus. Such serious accidents, as described by Austin,* with their attendant delay and expense, have led to a great deal of ingenuity being devoted to the provision of automatic tuyere valves which shall establish connection with the outer air the moment the blast pressure is taken off. One of the best of these is that of Eilers.† It consists of a simple box fixed against the back of the water jacket by means of patch bolts, the actual tuyere being simply the aperture in the jacket itself. The construction is evident from Fig. 74, in which V is a valve with planed face fitting the 3-inch tube in the back of the box air-tight by means of the pressure on its back and rather more than counterbalanced by the iron ball. When the pressure is removed this ball comes into play, and the valve, taking the position shown by the dotted lines, closes the blast pipe and opens the escape. In a line with the tuyere opening is the peephole provided with eyepiece as usual, and at the bottom of the box is a 3-inch hole for the removal of slag accidentally coming into the tuyeres, to which can be fixed a fusible plug, if desired. The whole arrangement is compact, though rather cumbersome and expensive, on which grounds it has not come into extended use. Other forms of patent tuyere boxes are described by Hofman.‡

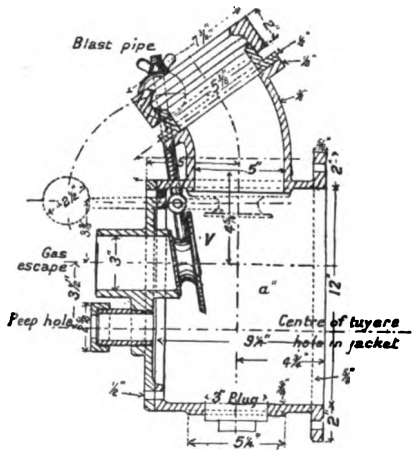

Fig. 74.—Tuyere.

* *E. and M. J.*, Dec. 15, 1894.
† Already figured by Hofman, *op. cit.*, p. 197.
‡ *Op. cit.*, pp. 198 and 199.

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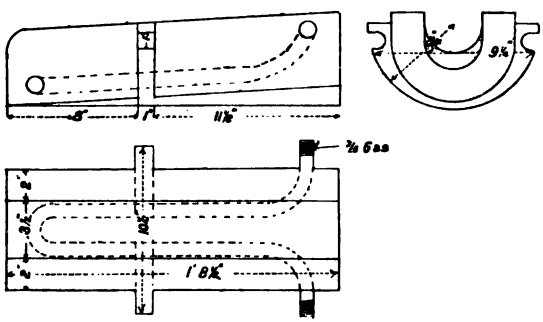
Water Jacketing to the Throat.—Copper furnaces being frequently water jacketed right up to the feed floor, the same principle has been tried in lead smelting, though with unsatisfactory results. The first furnaces of this kind erected were those of the *British Broken Hill Proprietary Company*, which are 40 by 120 inches at the tuyeres, the lower jackets being of cast iron and 20 in number—viz., 12 side jackets with tuyeres and 4 end jackets without (like Fig. 69). The upper portion of the furnace shaft is composed of four mild steel jackets, which have lugs rivetted on them by means of which they are supported by an I girder frame resting on hollow columns, which form a continuation of the ordinary lower columns.

The advantages of water jacketing the upper portion of a lead furnace were supposed to be:—(1) Greater durability through avoidance of relining; and (2) greater facility for barring off accretions. It was found, however, at *Broken Hill* that, through cooling of the upper portion of the furnace, the fuel consumption was slightly, but distinctly, increased, while the growth of "hangings" was actually encouraged by the presence of a cold surface to which they could attach themselves. The smoothness of the walls does somewhat facilitate the settling down of hangings, but not so much as might be expected; for, in any case, the "ring" of accretions has to be cut clean through in one or two places with steel bars before it can be got to settle down or break up, and this is the hardest part of the work. The upper jackets, moreover, were found to give considerable trouble through trickling, owing to their large size, and through leakage at the stay bolts; they have now been entirely abandoned. The furnace erected by Beardsley * at Zeehan, Tasmania, was practically a copy of the British Broken Hill furnaces, but the plant did not run long enough to enable the Broken Hill experience to be confirmed or modified.

Water-cooled Slag Spouts.—The wear and tear on ordinary



Figs. 75-77.—Water-cooled Slag Spouts.

* *Trans. A.I.M.E.*, vol. xxi.

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cast-iron slag spouts is so heavy that at a number of the leading American and Australian works water cooling is adopted, a bent ¾-inch gas pipe being placed in the mould when the spout is cast. A convenient form is that of the Broken Hill furnaces shown in Figs. 75 to 77.

HANDLING OF SLAG AND MATTE.

Arrangements have to be made not only for the disposal of the lead, but also for the far larger quantities of slag and matte produced in smelting. The oldest arrangement was to draw off matte, slag, and speiss indiscriminately into a tap pot, where they settled out into layers which could be separated easily after solidification. When this is done, below the slag is a cake of matte, and frequently at the extreme point of the cone a button of lead also, while if the charge contain much arsenic, so that speiss is produced, it will be found below the matte and above the button of lead.

Slag Pots.—An old form of slag pot is that shown in Fig. 78;* the wheel is of the compression-spoke type, the spokes being of wrought iron, the rim and hub of cast iron. Lubrication is always a difficulty with slag pots, even when plumbago is used, and, accordingly, modern slag pots are nearly always fitted with roller bearings,† the rollers being of cast steel from 3 to 3½ inches long and from ⅜ to ¾ inch diameter. The bottoms of the pots usually get worn through in about eighteen months, and to avoid throwing aside the pot as worthless, Terhune‡ devised a form with movable bottom, which is illustrated in Fig. 79. Another arrangement for worn-out bottoms, used at the *Parrot* Works (Butte, Mont.),§ is shown in Fig. 80. It consists of a cast-iron false bottom held in place by a countersunk ¾-inch bolt with large cup-shaped washer, if necessary. At the Parrot Works new pots are used for slag and worn-out ones with the false bottom for matte, producing a very flattened cone which is more easily broken up than the pointed form.

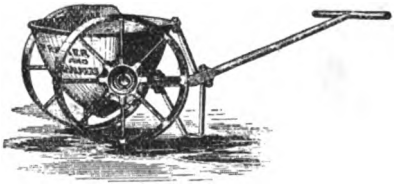

Fig. 78.—Slag Pot (old form).

All the above pots have the simple compression-spoke wheel which, according to the author's experience, so soon gets out of order that a plain cast-iron wheel properly proportioned is pre-

* From Fraser & Chalmers' catalogue. † *v.* the Terhune pot, Fig. 79.
‡ Terhune, *Trans. A.I.M.E.*, vol. xv., p. 92.
§ Keller, *Trans. A.I.M.E.*, vol. xxii., p. 574.

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ferable where a foundry is accessible, since it can be made just as light; it should have a ¾-inch wrought-iron tire shrunk on to protect the rim.* Another form of wheel is shown in Fig. 81

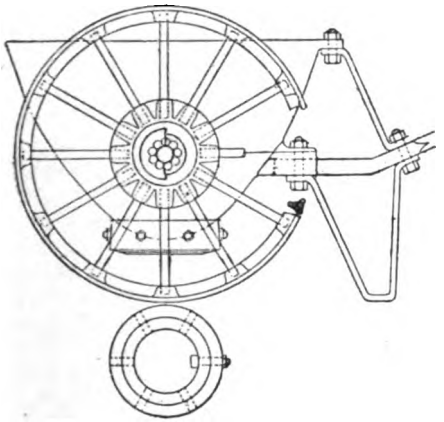

Fig. 79.—Slag Pot (Terhune's).

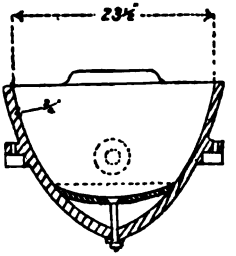

Fig. 80.—Slag Pot used at Parrot Works.

with alternate sockets,† and, perhaps, as good as any is that described by Keller,‡ and shown in Figs. 82 to 84. It consists of a cast-iron hub with wrought-iron spokes and tire, and, like most modern wheels, runs on steel roller bearings. The hub is tapped to receive the threaded ends of the spokes, which are of 1¼ inches round iron, and each of which has a jam nut to tighten it after the spokes have been adjusted to exactly equal length. The wrought-iron tire is shrunk on and fastened to the spokes by means of countersunk rivets. The splash guards, shown in Fig. 84, prevent the liquid slag from spilling on the hubs.

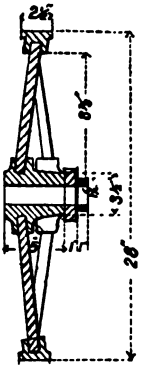

Fig. 81. Slag Pot Wheel.

When the slag is left to cool in the pots so as to be broken up and sorted by hand, a large number of pots are required (at least twelve for each furnace smelting 40 tons per day, or more in proportion to the increased capacity), and the wear and tear on them is very great, while the separation is very incomplete, many small shots of matte being retained by the slag. Most of the shots, however, are contained in the outer portion of

* Cast-iron wheels are used by the Broken Hill smelters at Port Pirie and Port Adelaide.

† Hofman, *op. cit.*, p. 248. ‡ *Loc. cit.*

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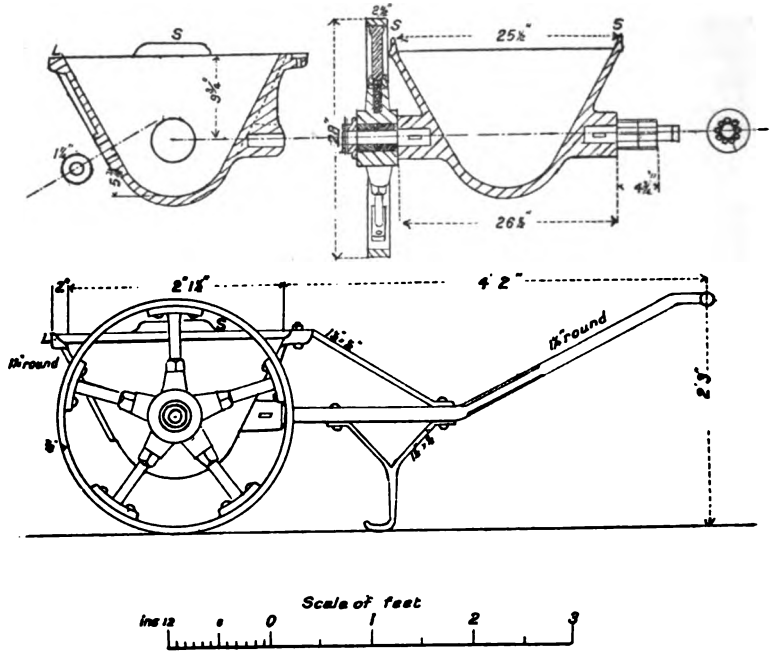
the cooled slag, the central core being much poorer, and upon this fact is based the catch pot or "tap pot" system of Devereux still in very common use. Figs. 82 to 84 show one very good form of catch pot with roller bearings and the Keller patent



Figs. 82-84.—Slag Pot.

wheels, the axles being fastened by wedges instead of by setscrews; besides the ordinary splash guards, S, it has a projecting lip, L, to take the wear in tipping. At 6 inches above the bottom is a taphole $1\frac{1}{4}$ inches in diameter, surrounded by a ring and rib reaching the projecting lip in order to protect the pot against injury when the interior slag is tapped by driving a square pointed $\frac{3}{4}$-inch steel bar through the cooled crust. In this way a crust of chilled slag is recovered for resmelting which contains most of the matte shots, while the cake of matte at the bottom of the pot remains undisturbed, even if still fluid, which it does not do when an attempt is made to pour out over the rim the interior fluid slag after the crust has solidified.

As regards the surface of the dump, some metallurgists recommend laying down tracks of narrow cast-iron plates for the

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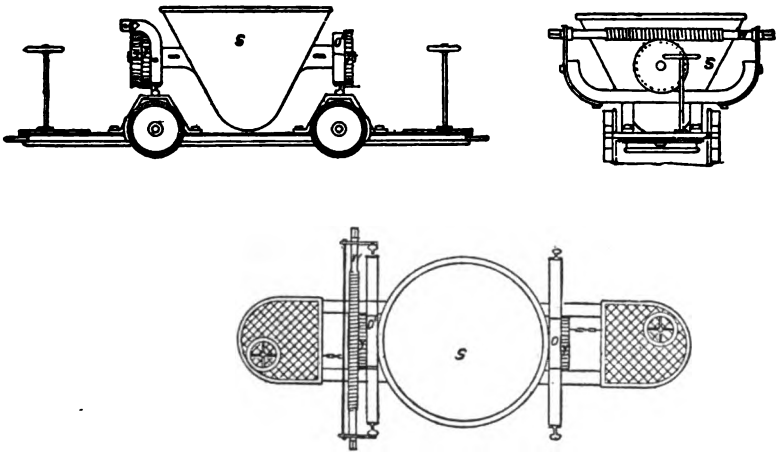
slag pots to run upon, in order to save labour in pulling the pots considerable distances. The ordinary way, however, to keep the surface of the dump smooth and hard is by levelling a series of squares about 3 feet across with pieces of sheet iron and filling with molten slag, this work being always kept up as the dump advances.

As the distance from the furnaces to the edge of the dump increases, handling in small pots becomes altogether too expensive, and it becomes necessary to use larger pots running on rails and drawn by horses or by locomotives. These larger pots are of two general patterns, single (*v.* Figs. 85 to 87) or



Figs. 85-87.—Large Slag Pot (single).

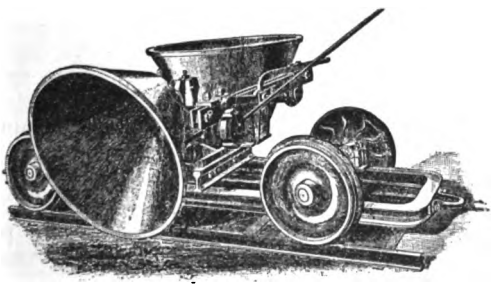


Fig. 88.—Nesmith Pot Truck.

double (like Fig. 88), which shows the Nesmith pot truck largely used in Colorado. Though of large capacity, however, this double pot takes up a great deal of space about the furnaces,

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and is, therefore, very awkward to introduce in many old works. The double pot truck of the Broken Hill Proprietary Company has a much smaller wheel base, which enables it to turn much sharper curves, and it is altogether the best device of the double pot style in use. Each pot holds about 18 cwts. of slag, and the trucks are handled by means of 5 feet turntables on steel rollers, one of which is placed in advance of each pair of furnaces.

Separation of Slag and Matte.—With the increase in viscosity of the slag caused by higher lime, alumina, magnesia, and zinc contents, and with the greater care in checking losses caused by keen competition among smelters, it became necessary to secure a better separation of slag from matte than is afforded by any of the above slag pots, more especially as the percentage of matte produced shows a constant tendency to increase of late years. The methods adopted may be divided into two main classes—A, Those in which the separation takes place quite away from the furnace; and B, those in which separation is sought to be brought about in connection with the furnace itself. Taking those of class A first, we have:—

1. **The Overflow Pot.**—This is usually more or less of the slag pot form, but much larger, and provided with a cast-iron spout through which the slag can escape after depositing the greater part of its matte. Sometimes a cast-iron cover is provided, but generally a simple crust of slag is allowed to form over the top to prevent rapid chilling of that below. The greater portion of the matte collects in the bottom of the pot, whence it may be tapped through a ring-protected aperture, like that shown in Fig. 82; or, if in insufficient quantity, by allowing the overflow pot to cool and breaking up its contents.

2. **The Exterior Forehearth or "Settler."**—This appliance, consisting in the main of a cast-iron box on wheels, is but seldom used with ordinary lead furnaces smelting ores, though commonly enough when concentrating matte. At the *Globe* (Denver) and several other progressive works, however, rectangular forehearths or settlers of very large size (up to 120 cubic feet capacity) have been installed with good results. For details of the appliances used in matte concentration, *v.* Part II.

3. **Large Crane-handled Settling Pots.**—The system in use at the *Grant* Works (Denver), and described by Austin,* is shown in Figs. 89 and 90. A series of five pits placed in position on the slag dump beneath an overhead track, which runs parallel with the front of the furnaces, contains each a large separating pot, about 5 feet diameter and 5 feet deep, fitted with trunnions and hooks, and holding 4 tons of slag. These pots are filled successively with slag produced in all the furnaces, which is conveyed to them in ordinary small pots, the shells of which are

* *Eng. and Min. Journ.*, November 23, 1895.

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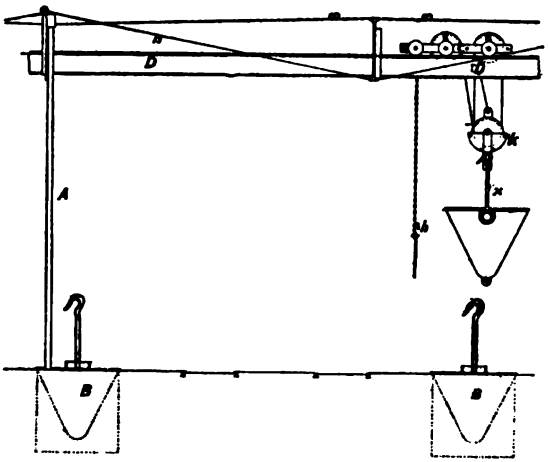

Fig. 89.—Large Slag Pot (double).

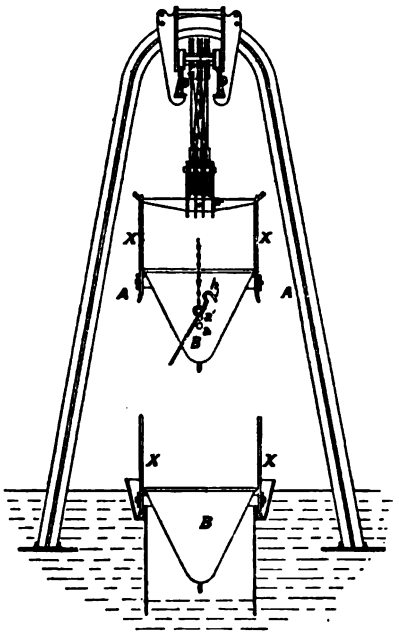

Fig. 90.—Large Crane-handled Settling Pot.

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set aside for resmelting. When each settling pot is full, it is allowed to stand from ten to fifteen minutes in order to allow the shots of matte to settle out, and then the overhead traveller, *c*, being brought into position over it and the block let down, the links, X, are hooked over the crossbar, and the pot raised by a steam winch. One of the slag cars, S, is then brought into position on the transverse track beneath, and the slag is tapped into it through one of the holes, *a* or a_1 (according to the amount of matte). The pot still containing the matte is then moved over another smaller slag truck (holding 1000 lbs. only), and the matte tapped out through another hole at the extreme bottom, together with any fluid slag left. The pot is returned to where the hook, *h*, can be inserted into the ring at the bottom by means of which it is inverted, and the shell of solidified slag turned out for remelting, after which it is again turned up and replaced in its pit for refilling. There are only two slag trucks to serve the five separating pots; they are hauled by a mule to the edge of the dump, and are easily tipped by means of a worm wheel, as shown in Figs. 85 to 87. When empty, a couple of shovelfuls of dry clay are thrown in, and they are again ready to take the charge of another separating pot.

4. **The Reverberatory Settling Furnace.***—Messrs. Iles, of the *Globe* Works (Denver), and Rhodes, late of the *Arkansas Valley* Works (Leadville), have worked on the principle of an external source of heat for keeping the slag perfectly fluid, so as to give the shots of matte a better chance of settling out. In both plans the reverberatory (which should preferably in a large works be duplicated to allow of cleaning out and repairing from time to time) is water jacketed, is situated at a distance from the furnaces, and has a separate fireplace with separate tapholes for slag and matte, the latter being low down on one side near the firebox, while the other is either on the opposite side (Rhodes) or at the far end (Iles).

In the **Rhodes separator** (Arkansas Valley) the slag from the furnaces is brought in hand pots and poured in through a lip at the end, the shells (10 per cent.) being returned for resmelting. The capacity of the furnace is 100 tons of slag, which comes direct from the slag tap of the furnaces, it being found that the ore-matte is required in order to collect and settle that carried by the slag in suspension. The slag is tapped every half hour into a train of Nesmith double-pot trucks drawn by a locomotive; the matte is tapped into hand pots and granulated for roasting.

At the Globe Works, where the **Iles separator** is used, the slag from the furnaces is tapped at intervals into a very large and long settling box of 120 cubic feet capacity with a side taphole for matte, which at these works is 8 to 12 per cent. of the

* *Private notes*, 1897.

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charge. The slag falls into double-pot trucks, which are pulled uphill away from the furnaces by a mule, drawn up by means of a steam winch and wire rope to a platform of I girders over the separating reverberatory, which has in its roof a square cast-iron hopper to guide the charge of molten slag. One of the blast furnaces is unprovided with settling box, and from it the whole of the slag and matte are tapped together and brought to the reverberatory for separation, the matte so brought amounting to 3 tons per day out of a total of 8 tons yielded by the reverberatory. The slag-matte is found to be 4 or 5 per cent. richer in copper and proportionately richer in lead and silver than the ore-matte. Both here and at Arkansas Valley the slags are very thoroughly cleaned by this appliance; at the latter works, before passing the separator, the slags average 0·9 per cent. Pb and 0·8 oz. Ag per ton; whereas after separation they carry on an average only 0·6 per cent. Pb and 0·5 oz. Ag per ton.

5. **Slag and Matte Taps.**—As examples of Class B, among separating devices, may be described the so-called "internal forehearths," or slag taps, of Matthewson and Eurich (in use at Pueblo and Aurora), and that used at Broken Hill. The principle in all is the same, namely, the addition to the front of the furnace of a cast-iron water-cooled or firebrick lined box, the bottom of which is open to the slag, while the inner side is formed of a water-cooled "damplate" or "tymp." The slag flowing under this diaphragm forms a quiet pool at, or about, the level of the tuyeres, thus thoroughly trapping the blast at all times, and overflows through a spout as fast as made into an ordinary settling pot, which catches any shots of matte carried over, and is changed every few hours. From this settling pot, the slag overflows into ordinary slag pots and is clean enough to throw away. As soon as matte is seen to come over with the slag from the upper spout a lower taphole is opened and a potful of matte allowed to run out.

The "internal forehearth," or slag tap, of Matthewson is illustrated in Figs. 91 and 92,* which show plainly the cast-iron damplate, B, with its $\frac{3}{4}$-inch gas pipe cast in, as well as the matte and slag spouts. Figs. 93 to 98 show the Broken Hill form of slag tap, in which the end jacket itself forms the back wall of the separating box, the front being formed of a single casting, bolted on and cooled by the usual $\frac{3}{4}$-inch gas pipe cast in.

This method of matte separation works most satisfactorily when the slags are fluid and do not chill too rapidly; very zinciferous slags, however, are not well cleaned, and in order to work satisfactorily the dimensions of the furnace should be such as to pass

* *Colo. S.S.M.Q.*, vol. ii., No. 1., p. 40; also *Min. Ind.*, vol. iii., p. 436.

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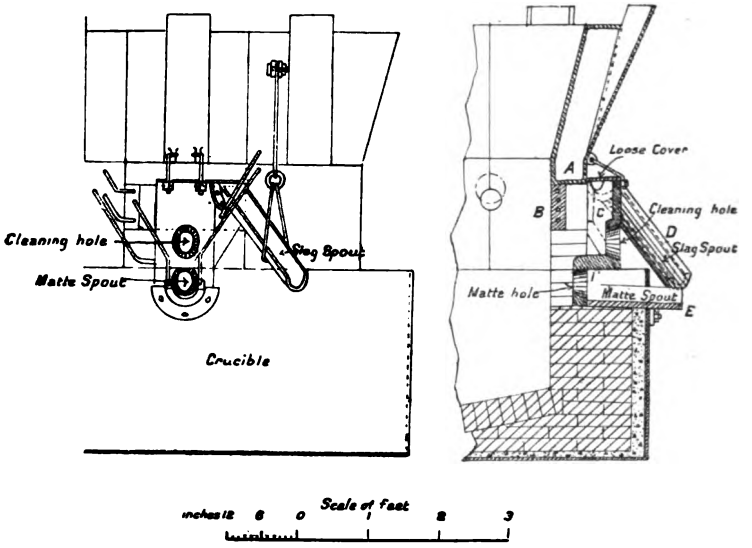
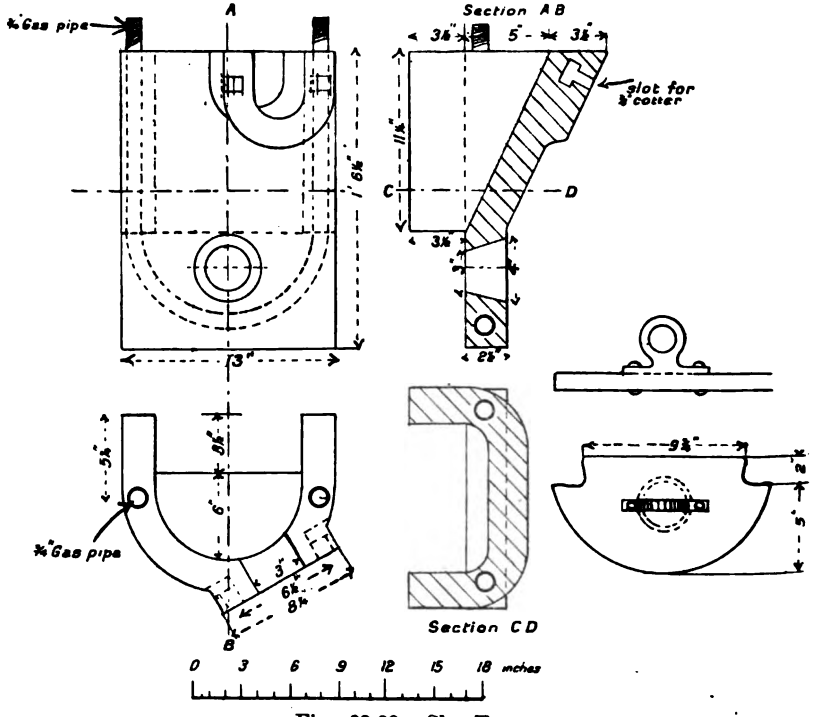


Figs. 91 and 92.—Matthewson Slag Tap.



Figs. 93-98.—Slag Taps.

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a minimum of 50 tons slag per twenty-four hours under the damplate.*

An additional precipitation of part of the metallic contents of the slag, whether held in solution or in suspension, can be obtained by adding scrap iron (preferably in the form of old tin cans, galvanised roofing, or other thin sheet scrap) to the "settler," through which the stream of molten slag passes. The iron acts by combining with sulphur or oxygen and precipitating lead, copper, and silver in the metallic form to be taken up by the shots of matte. This device was first introduced by the author when smelting copper and silver ores at Torreon, Mexico, in 1890, and was described by him in 1892;† but, according to Hofman,‡ it has been subsequently patented in the U.S.

CHAPTER IX.

BLAST FURNACE LEAD SMELTING—PRACTICE.

CALCULATION OF CHARGE.

Analyses of Ores and Slags.§—The first step towards making up a furnace charge is to ascertain the composition of the ores, especially as regards SiO_2, FeO, CaO, and ZnO, and, frequently, also Al_2O_3, BaO, MgO, and S. The methods used should be fairly accurate and at the same time rapid, for otherwise it becomes impossible to get analyses done within twenty-four hours after taking the sample, as should always be the case. As regards slags, rapidity is of vital importance, for the removal of some trouble connected with the working of the furnace frequently depends on ascertaining the composition of the slag being produced, and in this case a slag analysis to be of any use should be completed within a couple of hours or so. In order to secure this rapidity it is important to be able to decompose the slag with acid quickly and completely without a preliminary fusion. This can be always done, provided the slag sample is in a vitreous condition and very finely pulverised. Slag samples should be always taken by inserting an iron rod or small ladle into the potful of molten slag several inches deep, removing, and instantly plunging into a deep vessel of cold water, by which means the silicates are prevented from crystallising and remain

* Eurich, *Private communication*, May, 1896; this coincides also with the author's experience.

† *Proc. Inst. Civ. Eng.*, vol. cxii., pp. 151 and 192.

‡ *Min. Ind.*, vol. iii., p. 440.

§ *v.* Furman, *Manual of Practical Assaying*, N.Y., p. 79, *et seq.*; Hofman, *Metallurgy of Lead*, p. 274, *et seq.*: Croasdale, *E. and M. J.*, March 11, 1893.

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in the unstable vitreous condition. The final sample of 30 to 50 grammes should always pass a 120-mesh sieve, and the portion of a few grammes which is to be weighed out for analysis should be finely ground in an agate mortar. If this be done all lead slags and most lead and silver ores will be completely decomposed by boiling in HCl for a few minutes. Another essential condition of rapidity is the use of the smallest possible quantity of water and reagents.

The case of an **easily decomposed ore or slag** will first be considered :—

First portion for SiO_2, FeO.—Weigh 1 gramme of ore or 0·5 gramme of slag ground in agate mortar as above, mix in a porcelain dish with 2 c.c. water and a pinch of $KClO_3$, add 4 c.c. strong HCl and stir well, then 3 c.c. concentrated HNO_3 and evaporate to complete dryness. Add a few drops HCl and repeat evaporation to dryness, baking the residue well, but not igniting it to such a temperature as to decompose Fe_2Cl_6. Cool, add 10 c.c. strong HCl, break up the clots with a glass rod, *boil*, dilute, and decant through a very small filter. To the residue in the dish add 6 c.c. of a saturated solution of ammonium acetate, stir well, boil, settle a moment and decant through the filter. Repeat the washing with ammonium acetate twice, then pour the residue on to the filter and wash with small quantities of hot water until the last drop of the washings is tasteless. The residue is treated with a drop or two of ammonia water, rewashed, dried, ignited, and weighed. As a general rule, it may be calculated as SiO_2 with sufficient accuracy, especially in the case of a slag, but it may contain insoluble silicates of alumina and lime and traces of $BaSO_4$ (part of which, however, is dissolved in the concentrated HCl). If greater accuracy is desired, it may either be fused with alkaline carbonates, or evaporated to dryness twice with excess of HF, in which case any residue left is composed of insoluble silicates with some $BaSO_4$, the loss of weight being SiO_2.

To the filtrate from the insoluble residue add a few grammes of granulated zinc (free from iron) to reduce the Fe, run the solution through a small filter, add a few c.c. of H_2SO_4 and titrate at once with standard permanganate solution.

Second portion for $BaSO_4$, *check* SiO_2 and CaO.—Weigh 1 gramme of ore or $\frac{1}{2}$ gramme of slag, treat as above with water, $KClO_3$, HCl and HNO_3, then add a few drops of H_2SO_4. Evaporate to dryness, ignite gently, cool, boil out with 20 c.c. of water and ten drops of H_2SO_4, filter, and wash several times with hot water. Digest the residue with ammonium acetate several times, and then wash with hot water (this filtrate and washings should be saved separately, and will serve for a check wet assay for lead by the molybdate method already described.*

* *v.* Chap. i. p. 9.

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Wash the residue with two drops of ammonia water, and again with hot water, dry, ignite, and weigh as $SiO_2 + BaSO_4$. The difference between this weight and that of the SiO_2 obtained from the first portion may be considered as $BaSO_4$, or this residue also may be evaporated down with HF to get a check on the SiO_2.

Boil the filtrate, make alkaline with AmHO, add 5 c.c. AmHO in excess (to ensure the formation of sufficient oxalate to keep MgO in solution), then add a saturated solution of oxalic acid till the precipitate of ferric hydrate just redissolves on boiling. Boil for a minute or two, filter, and wash the precipitate on the filter several times with boiling water. Pierce the filter, wash the oxalate of lime into a 4-oz. flask with a jet of boiling water, pour 5 c.c. of dilute H_2SO_4 over the filter, and wash it all down into the flask, heat to boiling, and titrate immediately with standard permanganate solution, the standard for CaO being one-half of that for Fe.

A sample of readily decomposed ore or a slag can be easily analysed roughly for SiO_2, $BaSO_4$, FeO, and CaO in from one and a-half to two hours.

Ores containing Insoluble Silicates and much $BaSO_4$.—Take 1 gramme ore or ½ gramme slag, decompose with HCl, HNO_3, and H_2SO_4, evaporate to dryness and digest the residue with ammonium acetate to dissolve out lead sulphate, exactly as in the first method, after filtering off the soluble sulphates. Dry the residue and fuse either in a platinum crucible with Na_2CO_3 or in a large silver crucible with KHO for thirty minutes, disintegrate the fused mass in water, boil, filter, and wash well. The filtrate containing alkaline silicate may be evaporated to dryness twice with HCl and the residual SiO_2 filtered off, dried, ignited, and weighed; or, if the silica has been determined on a separate portion, this filtrate may be thrown away. Dissolve out the residue in 3 c.c. HCl and 10 c.c. water, boil, reprecipitate with a few drops of H_2SO_4, filter, wash dry, ignite, and weigh the $BaSO_4$. The HCl filtrate from the $BaSO_4$ contains the Al_2O_3, CaO, and other bases of the insoluble silicates; it may either be added to the first acid filtrate from the decomposition of the ore or the bases may be determined in it separately.

Alumina and *magnesia* may be determined in any of the foregoing portions by ordinary gravimetric methods.

Zinc.—Dissolve a separate portion of 1 gramme, remove the SiO_2 and Pb as above, peroxidise with $KClO_3$, add large excess of AmCl and AmHO, filter at once, and titrate the zinc in the cold filtrate slightly acidified with HCl by means of standard ferrocyanide solution, using uranium acetate as the indicator and pure ZnO for standardisation. With ores containing much iron the results are always low, owing to the obstinate retention of Zn by the iron precipitate.

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A rapid and very satisfactory way of determining zinc and lead in a single portion is the following :—

Dissolve ½ gramme ore in 10 c.c. of 1 to 3 H_2SO_4 and 5 c.c. strong HNO_3, boil down in a porcelain capsule till strong fumes of SO_3 are given off, cool, dilute to about 40 c.c., filter off the $PbSO_4$ and insoluble matter, from which the former is dissolved by am. acetate and titrated as usual with molybdate. To the filtrate add 200 grains potassium bitartrate, a *slight* excess of AmHO, and a little Fe_2Cl_6 (unless the ore contains 10 per cent. of iron or upwards). Titrate with ferrocyanide, using as indicator glacial acetic acid spotted on a plate, the end reaction, which is a sharp one, being indicated by formation of Prussian blue. The reaction differs from that which takes place in an acid solution, but appears to be quite uniform, and pure zinc oxide is used for standardisation. Manganiferous ores and slags should be dissolved in HNO_3 alone, evaporated to dryness and taken up with HNO_3 and $KClO_3$. Then filter off the insoluble matter, oxides of Fe and Mn, &c., through glass wool, wash with dilute HNO_3, dilute, and proceed as above.

Manganese is best determined in a separate portion of 1 gramme by Volhard's method, using sulphuric acid in the evaporation to separate Pb and Ba with the SiO_2, and then precipitating Fe_2O_3, Al_2O_3, &c., from the filtrate by means of an emulsion of zinc oxide in excess in a graduated ½-litre flask, the contents of which are then brought up to the mark with distilled water, and after thorough shaking allowed to settle. When the supernatant liquid is practically clear, 100 c.c. are, by means of a pipette, transferred to an 8-oz. flask, brought to a boil and titrated with standard permanganate, the standard of the solution for Mn being ·2964 of its standard for Fe. The error introduced by the volume of the precipitate of ferric hydrate with excess of zinc oxide may be usually disregarded, but, if necessary, a correction may be applied by weighing the precipitates from several determinations after washing, drying, and igniting, and calculating the volume of solution displaced.

Copper * may be determined either by the battery, by the iodide method, or by cyanide; in either case it should be first separated from the solution by precipitation with Zn (Al) or with sodium hyposulphite in a boiling acid solution. The electrolytic and iodide methods are preferable for high-grade copper products, but, according to the author's experience, no method gives more accurate results on ores than titrating against a "check" with cyanide, after previous precipitation with pure Zn or, preferably, Al.

* *v.* Torrey & Eaton, *E. and M. J.*, May 9, June 6, June 27, 1885; also Low, *Proc. Colo. Sci. Soc.*, vol. i., pp. 17, 69; Peters, *Modern Copper Smelting*, 1895, pp. 41-65, &c.

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Arsenic is best determined by Pearce's method.* The arsenic is precipitated as sulphide or as ferric arseniate, converted into alkaline arseniate by fusion with KNO_3 and Na_2CO_3, and precipitated as Ag_3AsO_4, which can be either reduced to Ag by a scorification assay and calculated back or determined direct by solution in dilute HNO_3 and titration with standard solution of ammonium sulphocyanate, after addition of ammonio-ferric sulphate to serve as indicator.

Sulphur is determined by ordinary methods, weighing as $BaSO_4$. The Iles method (fusion with KHO in a silver dish) gives as accurate results as any and is somewhat quicker than most.

A simple method of ascertaining *roughly* the amount of sulphur contained in a given ore is by determining the amount of matte formed on melting it with carbon, borax glass, and iron. Five grammes of ore are mixed with 15 grammes of borax glass and 3 grammes charcoal and two nails added. The mixture is then melted down in a hot fire for fifteen minutes, taken out and poured, after removing the nails. The button of matte produced is, when cold, carefully removed from the slag (and from the lead button, if any) and weighed. With copper-free ores it may be reckoned as 30 per cent. S., but with ores containing much copper or arsenic it is better reckoned as 25 per cent. S. The method gives only a rough approximation, but is very useful in works' laboratories pressed for time, as the determination of S by this means in ores containing not too much As is generally accurate enough for charge-mixing purposes as well as for checking the work done at the roasting furnaces. The amount of matte produced in the furnace is almost always less than that indicated by the above assay.

Calculating the Charge.†—It will be well to consider the most complicated case—viz., that of a custom works treating ores of very varying composition, including a large proportion of siliceous "dry" silver ores (*i.e.*, ores containing only a few per cent. of lead). At such works the ores, as received, are classified according to their composition, those which are regular supplies being invariably unloaded into stock bins, while odd lots (after sampling) are sometimes binned, but frequently made up into large "beds" of several thousand tons. A classification frequently adopted is the following:—To roaster bins, (1) sulphide lead ores; (2) pyritic and arsenical concentrates and fines for roasting and slagging. To smelter bins, (3) carbonate lead ores; (4) iron and manganese fluxing ores; (5) siliceous and high-grade

* *v. Proc. Colo. Sci. Soc.*, vol. 1; also Canby, *Trans. A.I.M.E.*, vol. xvii., p. 77.

† *v.* Newhouse, *S.M.Q.*, vol. ix., p. 373; Murray, *E. and M. J.*, Aug. 13, 1887, March 5, 1892; Furman, *S.M.Q.*, vol. xiv., p. 134; Hofman, *Metallurgy of Lead*, p. 209; also a paper by the author in *Proc. Civ. Eng.*, vol. cxii., pp. 133, *et seq.*

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ores. In this scheme all the odd lots, blendic, barytic, and somewhat coppery ores, as well as the bulk of the ordinary dry ores, are made up into "beds." Sometimes many more classes are made, as described in the author's paper cited below.

The first consideration must be whether there is or is not sufficient lead for separating from the other ingredients of the ore and for collecting the silver. There is no upper limit to the proportion of lead, for even pure roasted galena ores can be smelted in a blast furnace (though with heavy volatilisation losses); practically, however, the ore charge rarely, if ever, contains over 40 per cent. The lowest limit for good work is about 10 per cent. by dry assay, but there is considerable loss of silver with so low a charge, unless the ores are comparatively free from zinc. With impure and refractory ores the charge should contain at least 14 or 15 per cent. lead, and, as a general average, 12 per cent. by dry assay should be reckoned, the yield being about 80 per cent. The amount of silver in the ore should be such as to yield a "bullion" or work-lead of not more than 400 ozs. per ton. In Europe where "dry" silver ores are comparatively scarce the work-lead produced, except at Freiberg, rarely contains even one-half of the above amount. In the United States and Mexico, however, dry ores are so abundant that lead in blast furnace smelting is regarded more as a vehicle for the collection of the precious metals than as one of the two principal metallic constituents of the ores, and, therefore, the base bullion produced sometimes runs up even to 500 ozs. Even in Denver, however, a bullion of 300 ozs. is preferred, and it is only the scarcity of good lead ores which sometimes leads to the production of a higher grade bullion.

We will assume the case of a custom works classifying its ores received as follows:—

1. Lead sulphide ores and concentrates which are roasted* in whole or in part.
2. Auriferous and argentiferous pyrites, mispickel and coppery concentrates, and quartzose lead ores low in silver which are roasted together and then slagged, fluxing each other and giving a good product for the furnace.
3. High grade silver ores in quartzose gangue.
4. Odd lots of neutral, calcareous, siliceous, argillaceous, and other medium grade lead and silver ores, which are mixed together in a "bed," as they come in, with the object of making as few regular classes as possible.

It may be further assumed that under local conditions iron flux is scarce and dear, while impure limestone is cheap.

After analysing the different ores and ascertaining what

* With reference to the proportion of sulphide ores which must be roasted, a common rule nowadays is so to compound the charge that the production of matte will amount to 8 or 10 per cent. of the weight of charge—*i.e.*, for example, 10 to 12 tons of matte daily from a furnace averaging 120 tons of charge per day.

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amount of each is available, the first step towards calculating a normal charge is to figure MnO as FeO, and MgO and BaO as CaO. The atomic weights of Fe and Mn being so nearly alike the percentages of their protoxides are simply added together. Magnesia and baryta are reduced to their equivalent in CaO by multiplying by 1·4 and 0·4 respectively. When the quantity of zinc is small ZnO is also reckoned as CaO (× 0·7), but when large a separate calculation is better. The analyses modified as above are tabulated in the following form, the analyses of the fluxes available and that of the coke ash being added :—

TABLE XX.—Analyses of Charge Components.

Composition.	SiO_2.	FeO MnO.	CaO MgO BaO.	Al_2O_3.	ZnO.	Cu.	S.	As.	Pb.	Ag. Ozs. p. t.
Roasted ore,	10	27	2	...	11	0·5	6	...	35	50
Slagged ,,	25	40	...	...	2	3	2	2	16	30
Bed ,,	32	20	5	5	3	1	2	1·2	20	40
Siliceous ,,	80	3	3	2	...	...	0·5	...	1	100
Iron flux, .	10	75	...	...	...	...	...	...	...	...
Limestone, .	5	2	50	...	...	...	...	...	...	...
Coke ash, .	50	30	10	10	...	...	...	...	...	...

For the sake of simplicity the "ton" used is supposed to be the American "short" ton of 2000 lbs. We will suppose that the supply of these various classes of ore is approximately in the proportions given in the second column of the following table, which shows the number of lbs. of each constituent in a hypothetical preliminary trial charge supposed to be made up of the different classes of ore in the same proportion in which they are available in the stockbins or in the regular supplies :—

TABLE XXI.—Proportionate Weights of Charge Components.

Class of Ore.	Lbs. per Charge.	SiO_2.	FeO MnO.	CaO MgO.	Al_2O_3.	ZnO.	Cu.	S.	As.	Pb.	Ag. Ozs. per Charge.
		Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	
Roasted, .	200	20	54	4	...	22	1	12	...	70	5·0
Slagged, .	150	37·5	60	...	...	3	4·5	3	3	24	2·25
Bed, . .	250	80	50	12·5	12·5	7·5	2·5	5·0	3·0	50	5·0
Siliceous, .	100	80	3	3	2	...	...	0·5	...	1	5·0
Total, .	700	217·5	167	19·5	14·5	32·5	8·0	20·5	6·0	145	17·25
Average,	...	31·1	23·9	2·8	2·07	4·6	...	...	...	20·7	...

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From a consideration of the above totals, seeing that limestone is cheap and the zinc small in amount, it is evident that a high ratio of lime to iron will be most economical, while the combined amount of zinc and alumina, though not great, is sufficient to render it inadvisable to aim at anything above a monosilicate. The type slag No. 4 (p. 117) will, therefore, be a good one. With a slag so high in lime, and, therefore, of high melting point, it may be reckoned that nearly half the sulphur not appropriated by the copper will either pass into the slag or be eliminated as SO_2 (SO_3).

We will assume that the furnace is to take half-charges of 1500 lbs. on each side, out of which 200 lbs. or 13 per cent. shall be returned slag, and that each ore charge of 1500 lbs. is to be smelted with a fuel charge of 250 lbs. of inferior coke with 15 per cent. ash.

The complete calculation of a charge requires five separate computations:—

1. The copper present being all calculated to Cu_2S, how much metallic iron will be required to form FeS with half of the remaining sulphur?
2. How much metallic iron will be required to form Fe_5As_2* with the arsenic present?
3. How much iron ore is required to yield the above amounts of metallic iron?
4. How much flux is required for the coke ash?
5. How much flux is required for the ore mixture?

(1) **Sulphur.**—700 lbs. total ore contain 8 lbs. total Cu.

$$S : Cu_2 :: 32 : 126{\cdot}8\dagger = 0{\cdot}2524 : 1$$

8 lbs. Cu × 0·2524 = 2·02 lbs. S required to form Cu_2S.

But there are 20·5 lbs. S present, therefore one-half of the remaining 18·48 lbs. S is by hypothesis to be reckoned as combined with iron.

$$Fe : S :: 56 : 32 = 1{\cdot}75 : 1$$

9·24 lbs. S × 1·75 = 16·17 lbs. Fe required to form FeS (matte).

(2) **Arsenic.**—700 lbs. total ore contain 6 lbs. total As.

$$Fe_5 : As_2 :: 280 : 150 = 1{\cdot}86 : 1$$

6 lbs. As × 1·86 = 11·19 lbs. Fe required to form Fe_5As_2 (speiss).

(3) **Iron Ore.**—The required slag being $35SiO_2$ 27FeO, part of the iron in the flux is required to neutralise its silica.

$$FeO : SiO_2 :: 27 : 35\ddagger = 0{\cdot}77 : 1$$

10 per cent. SiO_2 × 0·77 = 7·7 per cent. FeO required to neutralise SiO_2.

The available FeO is, therefore, 75 − 7·7 = 67·3 per cent.

$$Fe : FeO :: 56 : 72 = 0{\cdot}\dot{7} : 1$$

Available Fe = available FeO × $0{\cdot}\dot{7}$ = 67·3 × $0{\cdot}\dot{7}$ = 52·34 per cent.

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* Not Fe_5As as given by Hofman, *op. cit.*, p. 212.

† According to the atomic weights.

‡ According to the percentages in the required slag.

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Total metallic iron required as above—viz., 16·17 lbs. for matte and 11·19 lbs. for speiss = 27·36 lbs. Putting x as the amount of iron ore required to yield this amount, we have

$$27{\cdot}36 : x :: 52{\cdot}34 : 100;\ \text{whence}\ x = 52{\cdot}3\ \text{lbs. iron ore.}$$

(4) **Coke Ash.***—When moderately good coke is employed, the error introduced by neglecting its ash is trivial, especially when the ash is not very siliceous; this calculation, therefore, is frequently omitted with good coke. This cannot be done, however, if the coke has much ash, and it is better to make the calculation once for all on an average sample of the kind of coke to be employed, and then use a constant calculated as below. The analyses show

Pounds.	Material.	SiO_2	FeO.	CaO
100	Coke ash,	50	30	10
x	Iron ore,	10	75	...
y	Limestone,	5	2	50

Let the percentages of SiO_2, FeO, and CaO in the chosen slag be represented by c, a, and b respectively. Then since $a + b + c$ is constant (= 90) we have

$$(1)\ \text{FeO} = \frac{a}{b}\,.\,\text{CaO};\ \text{and also}\ (2)\ \text{FeO} = \frac{a}{c}\,.\,SiO_2.$$

Now for the type slag No. 4, $a = 27$, $b = 28$, and $c = 35$.

From equation (1), substituting the figures of the analyses, we have

$$30 + 0{\cdot}75x + 0{\cdot}02y = \frac{27}{28}\,.\,(10 + {\cdot}50y);$$

simplifying we get $$x = 0{\cdot}62y - 2{\cdot}71. \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{I.}$$

From equation (2) $$\text{FeO} = \frac{a}{c}\,.\,SiO_2$$

$$30 + 0{\cdot}75x + 0{\cdot}02y = \frac{27}{35}\,.\,(50 + 0{\cdot}10x + 0{\cdot}05y);$$

simplifying we get $$x = 0{\cdot}028y + 12{\cdot}8. \quad . \quad . \quad . \quad . \quad . \quad \text{II.}$$

Then from I. = II. we get

$y = 67$ lbs. limestone
$x = 14{\cdot}6$,, iron ore
} required to flux 100 lbs. coke ash.

(5) **Fluxes for Ore Mixture.**—

Pounds.	Material.	SiO_2 per ct.	FeO per ct.	CaO per ct.
100	Ore mixture,	31·1	23·9	2·8
x	Iron ore,	10	75	...
y	Limestone,	5	2	50

$$(1)\ \text{FeO} = \frac{a}{b}\,.\,\text{CaO}$$

$$23{\cdot}9 + {\cdot}75x + 0{\cdot}02y = \frac{27}{28}\,.\,(2{\cdot}8 + 0{\cdot}50y);$$

* Slide rules and other mechanical devices have been invented to simplify this and the following calculations (*v.* Roberts-Austen, *Introduction to the Study of Metallurgy*, 1898, p. 247; also Wingham, "Discussion on Smelting Processes," *Proc Inst. Civ. Eng.*, vol. cxii., p. 206). They appear to be largely used in connection with iron blast furnaces, but the author is not aware that any appliance of the kind has ever been employed in lead smelting works. The necessary calculations are, after all, very simple.

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simplifying, $x = 0{\cdot}616\,y - 28{\cdot}27$. . . . . III.

$$(2)\ FeO = \frac{a}{c} \cdot SiO_2$$

$$23{\cdot}9 + 0{\cdot}75\,x + 0{\cdot}02\,y = \frac{27}{35}\,(31{\cdot}1 + 0{\cdot}10\,x + 0{\cdot}05\,y);$$

simplifying, $x = {\cdot}027\,y + {\cdot}136$. . . . . IV.

From III. = IV. we get

$y = 48{\cdot}23$ lbs. limestone
$x = 1{\cdot}44$,, iron ore } per 100 lbs. of ore mixture.

Thus to flux 700 lbs. of ore there will be required 10 lbs. of iron ore and 337 lbs. of limestone, making with the ore itself 1047 lbs.

We have already towards our charge the fluxes for the coke ash. 250 lbs. of coke at 15 per cent. ash gives 37·5 lbs. ash, which requires

Limestone, ...	25 lbs.	
Iron ore, ...	5 ,,	
	30 lbs.	
Also the slag charge is	200 ,,	
		230 lbs.

The difference between 1500 lbs. and 230 lbs. is 1270 lbs., which must be the combined weight of the ore and its fluxes in the charge.

Now 700 lbs. of ore require in all of fluxes:—

To flux silica as above, Limestone, .	337 lbs.	
,, ,, ,, Iron ore, .	10 ,,	62 lbs.
To form speiss and matte, ,, .	52 ,,	
Add weight of ore, ...	700 ,,	
Weight of ore and its fluxes, .	1099 ,,	

1099 x = 1270 gives us $x = 1{\cdot}156$ as the coefficient by which to multiply the above figures, and we have for our half charge:—

TABLE XXI*a*.—Composition of Furnace Charge.

	Fluxes Lbs.		Total.	In Practice.
	For Ore.	For Coke Ash.		
Roasted ore, . . .	809 lbs.	total.	231	230
Slagged ,, . . .			173	175
Bed ,, . . .			289	290
Siliceous ,, . . .			116	115
Iron ,, . . .	71	5	76	75
Limestone, . . .	390	25	415	415
Slag, ...	...	...	200	200
			1500	1500

The column headed "in practice" shows the charges actually weighed out, the furnace scale beams being usually set only to 5 lbs. If any portion of the ore or flux is wet, as, for example,

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the siliceous ore or the iron flux, allowance is made by adding on 5 per cent. or 10 per cent. (as indicated by the result of a special moisture sample) to the weight of that class of material. The total weight of charge will then run over 1500 lbs. The same is done in the case of wet coke. Table XXI*a*. shows the total number of pounds of each constituent in the combined half charge of 1500 lbs. ore, slag, and fluxes, and 250 lbs. coke. The total number of pounds of slag—viz., 1042—is found by adding together the number of pounds of SiO_2, FeO, CaO, Al_2O_3, and 90 per cent. of the ZnO, and allowing $3\frac{1}{2}$ per cent. extra for PbO, S, alkalies, &c. The amount of zinc going into the slag will vary a good deal, but, as a rule, from 10 to 20 per cent. will cover the amounts volatilised and carried into the matte. The coefficient for proving that the slag has been correctly calculated is obtained by $1042\ x = 1000$. The amount of lead in the charge (the total charge of ore and fluxes without slag is usually referred to) is 12·9, or, including the slag also, 11·2.

The quantity of matte is obtained by supposing the Cu_2S and FeS (already determined) to form 80 per cent. of it; the lead in it will not average more than 10 to 12 per cent., while the 8 per cent. remaining will cover zinc and other substances. The richness of matte in silver is generally calculated by supposing the lead present to be equally rich with the work-lead,* but this is only a rough approximation, and the matte is generally found to be richer than would be indicated by this calculation. The author finds that a much closer approximation to the amount of silver carried into the matte is obtained by reckoning that both the lead and copper contents of the matte are equally rich with the work-lead, except when the copper runs up to 20 per cent., above which point it seems to be only about two-thirds as rich as the lead. Such rules, however, are only approximations, and the amount of silver carried into the matte varies not only with the nature and amount of the other impurities present, but also according to the relative proportions of the two products.

The quantity and richness of the work-lead may be got at pretty nearly by reckoning that 3 to 5 per cent. of the lead present and 2 to 4 per cent. of the silver go into the flue-dust, while, unless some fume filtering process is adopted, even in good work with charges low in lead, some 8 to 12 per cent. of the lead and 1 to 3, or even 4, per cent. of the silver are lost in slags and in uncondensed fumes. These figures are, of course, based upon commercial assays, the true figures of corrected assays would frequently show much higher losses. The remaining lead and silver, less that accounted for in the matte, will be found in the work-lead. As average figures in the case under consideration we may suppose that 4 per cent. of the lead and 3 per cent. of the silver pass into the flue-dust, from which they are subse-

* Furman, *S. of M. Q.*, vol. xiv., p. 144.

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quently recovered, less the loss on re-treatment; while, say, 10 per cent. of the lead and 2 per cent. of the silver are lost. We have thus—

	Wt. in Charge.	Loss in Smelting.		Flue Dust.	Matte and Work Lead.
Lead,	167·6 lbs.	– 10 per cent. =	150·9 lbs.	– 5 per cent. =	143·4 lbs.
Silver,	19·92 ozs.	– 2 per cent. =	19·52 ozs.	– 3 per cent. =	18·94 ozs.

The Cu_2S with half the remaining S, as FeS, add up to 39·8 lbs.; as this forms 80 per cent. of the matte, the total weight of the latter will be 49·75 lbs., containing on an average, say, 12 per cent. or 6 lbs. of lead. There are left 143 – 6 = 137 lbs. of work-lead (about 10½ per cent. yield on the ore and fluxes) which contains about 276 ozs. silver per short ton without allowing for that in the matte.

The matte contains 12 per cent. lead and 16 per cent. copper, or together 28 per cent. of material as rich in silver as the work lead; therefore the matte at 28 per cent. of 276 ozs. will assay about 80 ozs. per short ton and remove about 2 ozs. of silver from each charge.

For the work-lead we have left 137 lbs. of lead, and 18·74 – 2 = 16·74 ozs. silver, corresponding to about 244 ozs. per short ton; the net yield of bullion being thus 15·5 per cent. on the ore alone or 10½ per cent. on the total weight of ore and fluxes.

No separate calculation is made for gold, since this metal is much more perfectly concentrated in the work-lead than is the case with silver, the matte containing relatively very little. So far from there being any perceptible loss in smelting gold ores, the gold obtained in bullion is usually in excess of the amount paid for or charged in the furnace books; most of the ores and iron fluxes carrying minute traces not accounted for.

The foregoing complete method of calculating a charge is only necessary at large works treating a variety of ores; in smaller works and in those which treat ores from only a single mine or group of mines, the calculation can often be simplified by leaving out of account the coke-ash, speiss, and matte, and adding a rough constant to the proportion of fluxes found for the ore charge in accordance with the result of practical experience. A simplified method of calculation on this plan is given in the paper on Smelting Processes already referred to,* and may be found useful by hard pressed metallurgists in charge of small plants. A further reason for using in practice a simpler form of calculation is to be found in the fact that the behaviour of sulphur in the furnace, and therefore the proportion of matte formed, depends very largely on furnace manipulation and particularly on the amount of blast used. If the atmosphere be distinctly reducing, as in the typical practice, the matte formed corresponds closely with the amount indicated by calculation;

* *Proc. Inst. Civ. Eng.*, vol. cxii., part ii., p. 135.

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TABLE XXII.—Tabulated Data for Charge Calculation.

	Dry weight.	SiO_2.		FeO (MnO).		CaO (MgO, BaO).		Al_2O_3.		ZnO.		Cu.		S.		As.		Pb.		Ag Ozs.	
	Lbs.	%	Lbs.	%	Lbs.	%	Lbs.	%	Lbs.	%	Lbs.	%	Lbs.	%	Lbs.	%	Lbs.	%	Lbs.	Per ton.	Per charge.
Roasted ore, .	230	10	23·0	27	62·0	2	4·6	...	...	11	25·3	0·5	1·1	6	13·8	...	...	35	80·5	50	5·75
Slagged ,, .	175	25	43·7	40	70·0	...	...	...	...	2	3·5	3·0	5·2	2	3·5	2	3·5	16	28·0	30	2·62
Bed ,, .	290	32	92·8	20	58·0	5	14·5	5	14·5	3	8·7	1·0	2·9	2	5·3	1·2	3·4	20	58·0	40	5·80
Siliceous ,, .	115	80	92·0	3	3·4	3	3·5	2	2·3	...	...	...	...	1	1·2	...	...	1	1·1	100	5·75
Iron flux ,, .	75	10	7·5	75	15·4	...	...	...	...	...	...	18·7 lbs. Fe				12·9 lbs. Fe		...	...	...	...
Limestone, .	415	5	20·7	2	8·3	50	207·5	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Slag, . .	200	35	70·0	27	54·0	28	56·0	2·5	5·0	3·5	7·0	...	...	...	...	...	...	...	...	...	...
Coke ash, .	37·5	50	18·7	30	11·2	10	3·7	10	3·8	...	...	...	...	...	...	...	...	...	...	...	...
Total, .	1537·5	...	368·4	...	282·3	...	289·8	...	25·6	...	44·5	...	9·2	...	23·8	...	6·9	...	167·6	...	19·92
		Total, 1042 lbs. slag.										About 49·75 lbs. matte, with about 80 ozs. Ag per ton.				About 20 lbs. speiss.		About 137 lbs. base bullion, with about 244 ozs. Ag per ton.			
Coefficient,	·09596	...	35·35	...	27·09	...	27·83	...	2·45	...	3·84										

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but if the blast be largely in excess of the quantity required to burn up the coke, as is the case occasionally in modern practice, sulphur may be very largely eliminated as SO_2. Even without varying the blast the production of matte varies according to the permeability of the charge, a closely-packed fine charge always yielding more matte than one of the same composition which is open and loose.

A still simpler method of calculating furnace charges consists in the use of a slide rule with slides for each base, specially graduated, so that equivalents of the different bases are measured by the same length. Such a slide rule is that devised by Wingham * with special reference to iron blast-furnace charges, but which can also be used for any kind of smelting, as it contains three separate silica scales—viz., for mono-, sesqui-, and bi-silicates, and base scales for lime, magnesia, alumina, ferrous oxide, and alkalies. On the back are other scales for sulphur required to form matte, iron-oxides to displace PbO and Cu_2O, limestone required to yield a given weight of lime, &c. With the aid of this simple apparatus the calculation of the basic or acid excess of any particular ore from its analysis is a purely mechanical operation occupying a few moments only; and, as already mentioned, this is practically all that is necessary except in very large custom works where great differences exist in the nature and proportion of the bases present, and where, therefore, it is necessary to know whether the basic excess or deficiency in any given ore is an excess or deficiency of iron or of lime.

FURNACE MANIPULATION.

This may be described under four heads—viz., "Blowing-in," "Blowing-out," Regular Smelting, and Irregularities in furnace working—all with reference to the large oblong furnaces already described.

1. **Blowing-in.**—The points to be observed in connection with this operation are, first, that the crucible of the furnace should be thoroughly dried out and heated red-hot before attempting the blowing-in proper; second, that it should be filled with hot molten lead as rapidly as possible to avoid crusting up the bottom; and, third, that the first slag which comes down should be ferruginous and as hot as possible, so that it may keep the lead hot and not form incipient top-crusts. The various methods of attaining this end by the use of bars of lead are described in great detail in the work of Hofman,† to which reference may be made with advantage.

When bars of lead for filling the crucible are not to be had—

* *Journ. Iron and Steel Institute*, part i., 1892, p. 233.
† *Metallurgy of Lead*, New York, 1893, pp. 219-224.

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as has happened to the author in Mexico*—the furnace may be started direct on specially high-grade lead ores, preferably carbonates, though thoroughly roasted and agglomerated galena ore would no doubt be equally efficient. In this case, after the crucible has been heated red-hot, first with several fires of good hard wood and then with charcoal, the lead-well and syphon-tap are thoroughly heated, and then a clay plug is put in the latter and the well is piled high with glowing charcoal. Upon the charcoal fire in the bottom of the crucible are charged large clean pieces of coke, which are turned over and over under a light blast through a length of 2-inch pipe, and as they ignite more coke is added till the whole crucible is filled with a glowing mass. The breast is then put in, large sticks of selected charcoal fed in to about the top of the jackets, and the furnace is then filled as rapidly as possible with alternate layers of coke and of the rich ore selected for blowing-in, to which just sufficient iron ore is added to form an easily fusible liquid slag.† As soon as the furnace is full, the flow of water through the jackets is increased and a *light* blast is turned on. The lead in this way comes down quite hot and sufficiently fast to fill the crucible in a very few hours; slag is tapped at intervals, and as soon as lead begins to run from the slag spout the lead well is cleared from charcoal, the plug in the syphon-tap is knocked out with a bar, and the furnace can be put on its normal charge. When care is taken in filling the crucible, not to get too much of the coke burnt away or clinkered, this method of blowing-in without using bars of lead can be made to give very good results.

2. **Blowing-out.**—When a furnace is in want of repairs or gets crusted up in the crucible; when some serious accident happens to the water supply; or when fuel or ore runs short, as occasionally happens, it is necessary to blow-out. This is done in the inverse way to blowing-in—viz., by stopping the regular ore charge and substituting slag with iron ore until the ore left in the shaft has been smelted out. The charge is then allowed to sink; the dampers leading to the dust flues in the case of furnaces with telescopic stacks being closed, while in the case of open-top furnaces the cast-iron coverplates are put on and luted down. When the charge has sunk so that flame begins to make its appearance on top, or even very heavy lead fumes without flame, the blast is shut off, the tuyeres taken out, the slag tapped till no more will run, the tapping jacket and breast removed, and the contents of the furnace are drawn. This is done by raking them out with iron hoes into a succession of wheelbarrows, which are taken away and cooled with water, the operation being finished by pulling down the front jacket and

* *v.* also Church, *Trans. A.I.M.E.*, vol. xvi., p. 611.

† All blowing-in charges should be made as ferruginous as possible, as the iron monosilicate slag is particularly fusible.

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raking out everything. Last of all, the molten lead in the crucible is ladled out into moulds.

3. **Regular Smelting.**—In regular work the charges are made up either by weighed quantities of ore taken from separate bins, the analysis of which has been previously determined, or from ore beds of several thousand tons, each composed of layers of ore of different compositions approximately in suitable proportions for the furnace. The former system has been described in a paper by the author* as employed at the El Paso Works (Tex.); the latter is the more usual system on the Continent of Europe and in most purely custom works. Most American works adopt a combination of both, stock-bins being used for certain large and regular supplies of ore, the composition of which varies only within narrow limits, while ore beds are made up with all the odd lots of ore received. In any case, fluxes are weighed separately. At some works the ore and fluxes are brought to the furnace in trucks and the fuel in wheelbarrows, more commonly both are handled in trucks; occasionally, wheelbarrows are used exclusively, though this is not to be recommended. When, as is now usual, the whole feed floor is composed of iron plates resting on I girders, ordinary trucks can be run anywhere; but when part of the floor is of wood or stone, a good arrangement is to use large wrought-iron handbarrows running on a pair of wheels, and resting during filling on legs between the handles and the wheels.

Weight of Charge.—All the items composing the charge must be accurately weighed into the truck or handbarrow. Almost invariably the multiple-beam scale is employed, with a separate beam for each kind of material composing the charge. The sliding weights on these being once adjusted, the front of the case is locked by the furnace foreman, and the beams are thrown in and out of gear one by one as required, by means of separate levers on the outside.

The absolute size of the charge is a matter for some consideration, for upon it, to some extent, depends the intensity of the reducing action. When carbonate or very thoroughly roasted ores are to be treated and the values concentrated into bullion with as little matte as possible (as at Broken Hill), a powerful reducing effect is essential, and small charges corresponding to only about 15 to 20 lbs. per square foot of section are preferred. When, however, much sulphides are to be used in the charge and a considerable production of matte is expected, the charges employed may with advantage be somewhat heavier, though never so large as in copper-matting or pyritic furnaces.

Method of Feeding.—In charging, fuel always goes into the furnace first, being followed by the ore mixture, with fluxes and slag on top; occasionally the ore fluxes and slag are mixed

* "Smelting Processes," *Proc. Inst. Civ. Eng.*, vol. cxiv., part i.

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together, which, however, as shown by Henrich,* does not give such good results on account of tending to form a fusible slag too high up in the furnace. The fuel should form an even layer over the whole area of the furnace, thicker, however, in the centre than at the sides, so as to make the centre of the charge more permeable than it would otherwise be to the current of ascending gases. As a rule, this is done by feeding most of the largest pieces of coke (and all the charcoal, if any is used) towards the centre line of the furnace, and then spreading the remainder of the fuel evenly over the whole area. Ore, fluxes, and slag should be spread evenly, except that the coarser parts of the charge are best spread first and the fines on top.

The presence of fine ore in the charge beyond a certain proportion (say one-fourth to one-third of the whole) is attended by many inconveniences. The first is a great reduction in capacity. A furnace smelting 80 tons per day, when nearly the whole charge is from nut to fist size or larger, will put through only half that quantity when the proportion of fine ore rises to 50 per cent. Another and more troublesome result is a choking of the furnace, which brings about an increase of pressure and an upward extension of the zone of fusion, in consequence of which so much of the fuel is consumed before reaching the tuyeres that there is not sufficient left to give the slag the necessary degree of fluidity for complete separation of matte. Perhaps the worst trouble of all in the old-fashioned low furnaces (though in modern high furnaces it is neither so frequent nor so serious) is a gradual sifting-down of fine ore through interstices between the coarser lumps, assisted no doubt by the vibratory motion set up by the blast, until in extreme cases barely warm fine ore pours into the tuyeres. Even when not reaching such an extreme, this sifting-down of fine ore is attended by the serious consequence of greatly increasing the loss of precious metals in the slag, since such fines as may reach the crucible and become carried away mechanically will be comparatively unaltered as regards their precious metal contents. Fortunately with modern high furnaces of ample area a much larger proportion of fines can be handled without serious trouble, than in the lower and smaller furnaces. Judgment must, however, always be used in feeding fine ore, a good rule being to make the layer thickest all round near the sides, throwing an extra shovelful or two wherever the fumes appear most dense. Irregular descent of the charges often indicates improper feeding. The indications of irregular working which can be noted on the feed floor are corroborated by the appearance of the tuyeres, which, in good work, should be covered by a thin scale of slag, through which the glowing interior should be visible in spots like stars. When a tuyere appears to be black it should be "rodded" with a bar so as to break away the short

* *E. and M. J.*, Dec. 27, 1890; June 6, 1891.

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nose which has formed, but if this returns very quickly and grows thicker, the remedy is indicated in a subsequent paragraph.

Pressure of Blast.—The blast-pressure should be watched by means of the gauge on the blast pipe of each furnace, which should be constantly compared with the gauge at the commencement of the blast main just outside the blower room, and the quantity of air given regulated accordingly. Some furnacemen are accustomed to treat the blast gauge as a mere means of regulating the quantity of air which they supply to the furnace, and to continually close the furnace blast-gate when the pressure rises and open it again when the pressure falls. This plan has the great disadvantage that precisely when the furnace from any cause gets clogged up and requires more blast to push through the obstacle actually less is received, while when it is smelting well and the mass of material in the shaft is in good loose condition so much blast will be put on as to drive the heat up. A better plan is to determine by repeated trial the volume of air at given pressure which a furnace of given dimensions will take when burning coke at a given rate, and, instead of continually fiddling with the blast-gate, to keep the volume of air supplied as nearly as possible constant. This is most easily done when each furnace has its own blower, for it is only necessary to run the latter at a constant rate of speed; in the usual case of a general blast main supplying a row of furnaces it is much more difficult, because an increased resistance on any one furnace automatically diminishes the volume of air passing through. By keeping the volume of air as nearly as possible constant, the blast-gauge becomes a delicate barometer, showing the changes which are going on inside the furnace, and in conjunction with the other signs visible at the tuyeres and on the feed floor indicating the remedy to be applied.

In all furnaces, except those with continuous slag-flow, the quantity of slag in the furnace between the slag spout and tuyere levels is under the control of the tapper, who once or twice in a shift usually allows the slag to rise to the tuyeres, and quickly taps it out to see the quantity in the furnace, less than the normal amount indicating the formation of incipient crusts. The depth of the pool of slag and matte below the slag spout depends entirely on the height to which the lead is allowed to rise in the lead well. Every now and then it is allowed to rise higher than usual, by dipping nothing out, by which means matte and speiss rise to the level of the taphole and can be tapped out, flushing with them any incipient crusts on the level of the lead bath; the lead is then dipped or tapped from the lead well, and comparatively clean slag can be tapped for some time. It is very important to keep the level of the lead in the well as high as possible, especially when smelting a charge low in lead, for in this way the surface of the lead in the crucible is

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also brought nearer the tuyeres, and the matte and speiss are not so liable to chill. Of course, the higher the level of the lead the more is the separation of matte from slag hindered, but this does not matter when one or other of the methods of outside separations described in chapter x. are adopted.

Working Force.—The number of men required per shift by a furnace from 33 to 42 inches at tuyeres, and 96 to 140 inches long is, *above*, one feeder and two or three charge wheelers according to the daily output of the furnace; *below*, one "furnace keeper" or lead moulder, one slag tapper, and two to four pot pullers or slag men, according to the distance the slag has to be taken, and the nature of the arrangements for handling it. Besides these, there will be required a variable number of labourers on the dump, for breaking up and sorting slag, &c.

Irregularities in Furnace Work.—Some of the irregularities in furnace work, and the modes of rectifying them, are as follows:—

1. **Dark Tuyeres with Long Noses.**—The nose is melted off by closing the valve of the tuyere in fault, so that the heat from its neighbours can creep close up to the iron at that point. The same remedy is adopted when stones of ore present themselves at one or two tuyeres; when stones or fine ore appear at several tuyeres at once, the remedy is to run down the furnace a few feet and fill up rapidly.

2. **"Hot-top" (over-fire, fire-tops).**—This is a very common incident, especially in low furnaces, and may be caused by irregular descent of the charges; by too much fine ore in the charge, or by its uneven distribution; by too great blast pressure; or by wall accretions. It is usually treated at first by running down the furnace a few feet, and filling up rapidly with cold charges, adding an extra amount of slag over the hot places; but if the defect persistently recurs after a repetition of this treatment, the remedy must be sought further, probably in the removal of wall or hearth accretions.

3. **Uneven Descent of Charges.**—This is usually accompanied by dark tuyeres on the "hanging side," and is often the result of bad feeding. The remedy is to feed more fuel on the hanging side, and more ore-mixture on the quickly descending side, while part of the stream of water may be turned off the jackets on the hanging side. Should this not have the desired result, a heavy 1½-inch octagonal steel bar is driven down into the hanging part of the charge to loosen it and break up any half-fused masses. In charges containing much zinc it is preferable to drive down the bar at once so as to break off any incipient accretions.

4. **Obstruction of the Syphon-Tap.**—This may be caused by (*a*) lead sulphide held in solution in the lead separating out on cooling; (*b*) copper in the lead acting similarly. The temporary

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remedy is to chisel out the bottom of the well containing the lead and insert into the channel a succession of thick iron bars heated red hot. The permanent remedy is a slight alteration in the charge. Sulphide in the lead indicates a lack of reducing power caused by a want of heat in the smelting zone, and may be cured by adding a little more fuel, or, sometimes, by adding more iron flux or by slightly diminishing the blast. Copper in the lead points to the necessity of adding more sulphide ore to the charge, so as to carry it into the matte.

5. **Wall Accretions or "Hangings."**—In the charges of many modern lead furnaces, which run so high in zinc, the growth of wall accretions is at once the most serious and the most commonly recurring of all furnace troubles. Besides contracting the furnace area and, therefore, reducing its capacity, they always cause irregular descent of the charges, and increase the amount of flue dust formed, through the concentration of the blast over a smaller area; while they generally cause a "hot-top," and grow so fast after once starting, that if neglected on a high zinciferous charge, they inevitably cause the furnace to be blown out. As soon as they begin to cause irregularities they must be detached, an operation known as "barring down." At some works it is customary, when treating a very zincy ore-mixture, to drive down a long steel bar in the four corners of the furnace once every twenty-four hours, with the object of detaching incipient crusts; in others, each furnace is let down several feet every two or three days, or in extreme cases, even once daily with the object of tracing more clearly the growth of these accretions. The usual place, however, for hangings to form is about a couple of feet above the jackets, from which point they rapidly grow upward.

The removal of the hangings may be accomplished either by smelting them out or by dragging and lifting, or by both methods combined. The actual barring down is done as follows:—The furnace is fed down slowly with a slackened blast till the charge has reached the top of the jackets, no lead being drawn from the well meanwhile, so that the crucible may be full of lead, which is kept hot by the coke floating on it. The blast is then stopped entirely, the tuyeres closed, the supply of water to the jackets nearly cut off, and the whole of the slag tapped out. A double charge of coke is then thrown into the furnace, with some slag and iron flux, so as to form a bed for the dislodged material to fall upon. The cutting out of the accretions is then commenced from the bottom upwards by means of square-pointed $1\frac{1}{4}$- to $1\frac{1}{2}$-inch steel bars 16 feet long, which are driven with sledges into the crust just above the jackets from the opposite side of the feed floor. As pieces of the hangings are broken off, charges of fuel, slag, and fluxes are added, if the material is to be smelted out in the usual way, until the whole

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of the crusts have been cut off, when smelting is again started under a light blast, keeping the level of the charges low for an hour or two. Once broken up, the hangings will frequently "smelt out" with great rapidity, and the slag needs to be tapped very fast. If a crust has formed on top of the lead it is broken up as far as possible with a steel bar through the taphole before turning on the blast, and soon smelts out, especially if a few bars of lead or a large charge of dross are thrown into the furnace on top of the crusts, so as to come down hot and help to heat up the crucible.

If it is preferred to rake out part of the crusts, this is done by cutting away part of the bricks between the jackets and the deck frame. The broken up accretions are then raked out and sent either to the roasting furnaces, to the fuse box of a slagging roaster, or to a separate smelting reverberatory; the opening is bricked up, a few slag charges given, the furnace filled with the ordinary charge, and the blast turned on again for regular work. "Smelting out" is, however, usually preferred as being simpler and cheaper.

6. **Hearth Accretions or "Sows."**—The formation of accretions or crusts on top of the lead is indicated by the descent of the charge in jerks accompanied by sudden bursts of flame, sparks, or even puffs of smoke; and by the lead in the well becoming dark and cold, and ceasing to "play" with the blast. The position and extent of the crust can generally be determined to some extent by inserting iron rods through the slag taphole. The most usual form of crust is one which begins at the back of the furnace and gradually grows towards the front, cutting off communication with the crucible and forcing the lead to run out with the slag. The usual cause of hearth accretions is a wrongly calculated charge, and a slag analysis will generally supply the key to the trouble. It is here that the value is seen of rapid methods which give fairly accurate results in an hour or two. In the meantime all that can be done is to give a slag charge now and then, and to slacken the blast so as to give a high temperature at the tuyeres, drawing as little as possible from the lead well, so as to keep the level high, and breaking up the crust as much as possible by driving in steel bars through the taphole and down through the mass of charge from the feed floor.

Generally, by this means and by an appropriate alteration in the composition of the charge, the crust can be smelted out, but sometimes it will not yield to such treatment, and has to be removed from the furnace bodily. To do this, the blast is stopped and the tuyeres taken out, the openings in the jackets plugged with clay, and, after passing heavy steel bars through opposite tuyeres near the front of the furnace to hold up the mass of charge, the breast or tapping jacket is taken down.

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The cold slag in front is chipped away and a little of the charge raked out, balls of clay being rammed up under the front jacket to prevent the remainder from coming down. After ladling out the pool of lead, which will be found in the front of the furnace, the crust is exposed and broken up by starting a hole in it with a 1¼-inch square-pointed steel bar, and then wedging it up in pieces by means of heavy 2-inch bars. After breaking up as much as possible of the crust and raking it out, the clay is removed, the space in front filled with charcoal or coke, and the breast jacket replaced; after which the steel bars through the tuyeres are pulled out, the clay stoppers in the tuyere holes replaced by the tuyeres, and a gentle blast is let on. The lead ladled out, together with a few more bars, is added to the top of the charge, and smelting is resumed in the normal way, except that the taphole requires to be frequently "rodded," in order to keep open the communication with the lead in the crucible.

7. **Cracked Jackets.**—A cracked jacket will often produce a crust on the lead; although the crack may be sometimes temporarily stopped by throwing balls of bran or of fresh horse-dung into the water feeders of the jacket, this can be only a temporary remedy. A burnt wrought-iron side jacket requires the blowing out of the furnace for its replacement, but a cracked cast-iron "section" or end jacket can be easily replaced in the following way:—First, a full stream of water is turned on, so as to cool it and thicken the crust of chilled slag lying against it, while two courses of brick are chiselled out above. Next, the blast gate on the branch blast pipe is closed, and the water supply of the cracked jacket is shut off. It is then propped up temporarily, unbolted from its fellows, and taken down, a new one being put into its place after carefully cleaning the seat from chilled slag. Should the melted slag break through the crust, it can be stopped by a clay ball, and by playing on the crust for a moment with a hose, if necessary.

Furnace Book-keeping.—Careful account must be kept of the work done in the furnaces, debiting to them the quantities of metals in the charge as shown by the weights and assays, and crediting the products turned out. Hofman* quotes a convenient blank form for these accounts.

* *Op. cit.*, p. 243.

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CHAPTER X.

BLAST FURNACE LEAD SMELTING—PRODUCTS.

It has already been seen that the principal products of lead blast furnaces are four in number—viz., (1) **Work-Lead**; (2) **Matte**; (3) **Speiss** (not often produced); and (4) **Slag**; besides which secondary products, such as **wall and hearth accretions** and **flue dust**, have to be taken into account.

1. WORK-LEAD.

Work-Lead or "Base-Bullion."—The lead produced in the furnace may be either ladled into moulds direct from the lead well, or tapped from it into a movable cooling pot, from which it is ladled into moulds of thin cast iron (with the name of the works in raised letters on the bottom) of the shape shown in Fig. 99.* They are whitewashed to prevent sticking, and hold

Fig. 99.—Mould.

on an average about 110 lbs. each; they must be carefully warmed the first time of using, but the heat of the lead keeps them afterwards at the right temperature. At *Tarnowitz* similar moulds are fixed upon a link belt which is moved by hand power as required, the cooled bars being dropped on to a truck below the axle carrying the belt. At the *Globe* and some other works the row of moulds is placed side by side on a long car which is pushed transversely across the stream of metal tapped from a cooler.

Comparing tapping with dipping the latter has the advantage that the level of the lead is kept more even, by which the tendency to form a crust is lessened; it is, therefore, preferable when the percentage of lead in the charge is as low as 8 per cent. and also when the lead is to be sold to independent refining works, as in that case it is advantageous to mould a good proportion of the dross together with the lead without skimming. When, however, the refinery and the smelting works belong to the same proprietors, it is generally preferable to tap the lead

* From Messrs. Fraser & Chalmers' catalogue.

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into a cooling pot in which the dross is skimmed off to be returned to the furnace, where its copper contents can be taken up by the matte, and from which the skimmed lead can be ladled at leisure into the moulds.

Except gold and silver, all the foreign substances present appear to collect during cooling in a dross which rises to the surface. When the lead is very impure the irregular distribution of this dross (which is always poor in silver) may give rise to a very irregular distribution of silver in the different parts of the bar. When the lead is not under 98½ per cent. the silver is pretty regularly distributed throughout it, the bottom and ends being richer than the upper portions, and the centre of the sides being the richest of all. Raht, in an elaborate article,* shows that the distribution of silver in the bars follows the rate of cooling, and that, contrary to what might be expected from a consideration of the Pattinson process (*q.v.*) though quite in accordance with the melting points of the two metals, those parts of a bar which solidify first are the richest in silver, while the lowest silver contents are in that part which cools last—usually the centre of the upper surface. The question of the distribution of the silver depends on the formation of a fusible *eutectic* alloy of silver and lead, which cannot be considered in detail here.

The irregularity in composition renders necessary special precautions in sampling. A very good way is to saw the bars across and take the sawdust as sample, but the more usual way is by means of a long-handled, hollow, spherical mallet fitted with a movable punch, which is simply driven about 2 inches into each bar of lead by a single blow, the chips being forced back into the hollow mallet, whence they are removed at intervals. The usual system is to take a row of five bars face upwards and drive the punch into each in a diagonal line from the far end of the first to the near end of the fifth; then, turning the bars over, another sample is taken from each along the opposite diagonal. If the holes are correctly spaced (which after a little practice can be done with great rapidity) the sample will be very nearly accurate. The chips from each truck load of bars (say 10 to 15 tons) are melted down in a plumbago crucible, well stirred with an iron rod, and poured into a mould. The resulting sample bar is drilled completely through in three or four places, or is sawn across in two places, the sawdust being taken as the final sample.

Another method of sampling recently adopted at a leading American works, according to Hofman,† consists in sawing into each bar by means of a circular saw provided with stops so as to prevent the cut going more than halfway across. The cuts

* *Mineral Industry*, vol. iii., p. 414. † *Ibid.*, vol. iii., p. 425.

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are taken alternately from near the ends and from the middle and the sawdust is mixed as a sample.

In the assay *very* impure bullion may require some scorification, but with ordinary bullion simple cupellation at a low temperature is sufficient. The distribution of silver in an ingot of lead has been elaborately worked out by A. Claudet.*

Composition of Work-Lead.—The following Table XXIII. gives analyses of work-lead or base-bullion from different places:—

TABLE XXIII.—ANALYSES OF WORK-LEADS.

	Freiberg, Saxony.	Mechernich, Rhen. Prussia.	Przibram, Bohemia.	Andreasberg, Upper Harz.	Leadville, Colo.	Broken Hill, N.S.W.
Reference,	1.	2.	3.	4.	5.	6.
Pb, . .	95·088	99·5913	97·3597	98·91053	99·079821	96·5900
Ag, . .	0·470	0·0215	0·4230	0·09300	0·611244	1·0730
Au, . .	und.	tr.	tr.	...	0·000388	0·0007
Bi, . .	0·019	...	0·0070	0·01955	tr.	none.
Cu, . .	0·225	0·1332	0·1100	0·03473	0·047910	0·8200
As, . .	1·826	...	0·2900	0·06520	?	0·3800
Sb, . .	0·958	0·2180	1·5240	0·38858	0·213894	0·7100
Sn, . .	1·354	...	0·2500	0·17149	tr.	none.
Cd, . .	none.	...	...	tr.	tr.	...
Fe, . .	0·007	0·0300	0·0036	0·00544	0·006300	0·0200
Zn, . .	0·002	0·0060	0·0012	0·00161	0·001605	tr.
Ni, . .	...	tr.	0·0015	0·00630	...	none.
Co, . .	...	...	...	...	...	...
S, . .	0·051	und.	0·0300	und.	und.	0·1400

References.—1. Hofman, *Met. of Lead*, 1893, p. 244. 2. *Berg- u. H. Zeitung*, 1886, p. 434. 3. *Oesterr. Jahrbuch*, vol. xxxix., p. 52. 4. Emmons, Geology and Mining Industry of Leadville, *Mon. XII. U.S. Geol. Surv.*, p. 694. 5. Hofman, *E. and M. J.*, Oct. 21, 1893. 6. *Private notes.*

2. MATTE.

Composition.—The mattes formed in lead smelting are mixtures of various metallic sulphides, iron almost always predominating, but replaced more or less by lead and copper, and to a smaller extent by Zn, Ni, Co, Mn, Ag, As, Sb, and Ba; other occasional constituents being Ca, Mg, and Bi. At Broken Hill, where the ores contain but little iron and are smelted quickly at a low temperature, the matte consists chiefly of PbS and ZnS. The proportion of copper in the matte depends on that contained in the ore, for nearly the whole of it goes into

* *Proc. Inst. of Mining and Metallurgy*, Oct., 1887.

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the matte. The percentage of lead in the matte depends almost entirely upon the reductive power of the furnace, which in its turn is chiefly affected by its height and by the fusibility, or otherwise, of the charge. Generally speaking, the higher the furnace, and the higher the melting point of the slags, the lower will be the percentage of lead in the matte.

It is generally supposed that iron exists in mattes as FeS, and this is no doubt the case as regards the greater portion of it. Chemists, however, for a long time have been well aware of the existence of magnetic iron oxide in mattes, although the fact has been to a great extent ignored by metallurgists. Guyard * found 16, and even 23, per cent. of magnetite in some Leadville mattes, and supposed them to contain Fe_3O_4 as a normal constituent, formed by Percy's reaction—

$$FeS + 10Fe_2O_3 = 7Fe_3O_4 + SO_2;$$

but there would seem to be some doubt as to the accuracy of his analytical methods. Hampe's published analyses of matte, however, always show oxygen as magnetite, and the author's analyses of Rio Tinto matte in 1884-5 showed from 4 to 6 per cent. of Fe_3O_4 insoluble in dilute nitric acid. According to some papers by Ed. Keller † it appears that the presence of magnetite is almost universal, but the lower the copper contents are, the more abundant is the magnetite.

As to the condition of the remaining iron it has been frequently observed ‡ that, after calculating the other metals present to their respective sulphides, there is not sufficient sulphur left to form FeS with the remaining iron, and this is true, even if we allow for the iron present as magnetite. In the Rio Tinto matte, for instance, after calculating the 43·11 per cent. of copper to Cu_2S, and the 1·373 per cent. of Pb, Zn, Ag, Bi, Mn, Ni, Co, and As, to their respective sulphides, the sulphur remaining is insufficient to form FeS with the iron, of which, after allowing for the 6·25 per cent. of magnetite, some 6·14 per cent. remains in excess. This excess of iron has been supposed to exist as a subsulphide, but the author adheres to the view of Münster and Schweder—viz., that it exists in the metallic condition simply dissolved in the metallic sulphides. From 10 to 16 per cent. of metallic iron is found to exist in the blast furnace matte produced by smelting roasted pyritic ores at Zalathna (Transylvania),§ great part being in the form of distinct shots up to the size of a bean. On the other hand, Pearce has described‖ some reverberatory mattes rich in both

* Emmons, *Mon. XII. U.S. Geol. Survey*, 1886, p. 724.
† *Colo. S.S.M.Q.*, Dec. 1893; and *E.M.J.*, Nov. 16, 1895.
‡ Hofman, *Metallurgy of Lead*, p. 253.
§ Farbaki, *B- u. H. Zeitung*, 1894, p. 177, *et seq.*
‖ *Trans. A. I. M. E.*, vol. xviii.

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copper and lead in which the proportion of sulphur appears to indicate that the iron present exists as Fe_2S_3; this, however, cannot be considered as proved. It is, however, certain, as pointed out by Keller, that as regards the composition of ordinary mattes containing under 20 per cent. Pb and from 1 or 2 up to 40 or 50 per cent. Cu, the only thing constant is the percentage of sulphur, which varies between the narrow limits of 22 and 25 per cent. This percentage appears to be a sort of critical point for mattes beyond which sulphur cannot be oxidised out without iron going too. The percentage of sulphur remaining nearly constant, wide variations in the proportions of copper and lead are counterbalanced, not only by variations in the amount of iron present, but also by differences in its mode of combination. When the amount of iron is low, part may exist as Fe_2S_3; when high, a portion is always found as Fe_3O_4, and generally another portion also as free metallic iron. In the case of mattes very rich in lead it is probable that in some cases metallic lead is present, being simply held in solution in the bath of sulphides.

Analyses of blast furnace mattes from lead smelting works are given in Table XXIV., some of them being re-calculated from the data given so as to show the mode of combination of the iron. Two copper mattes are added for comparison.

The first mattes produced in blast furnaces from mixed charges low in lead, rarely contain over about 5 per cent. copper, and 10 to 15 per cent. lead, though they may carry more lead if the furnace is run at too low a temperature. It is worthy of note that lead mattes are always very poor in gold, which is much more perfectly concentrated in the work-lead than is the case with silver. The amount of the latter metal contained depends primarily on the grade of bullion produced and on the amounts of lead and copper present; the matter has been already discussed in a previous chapter.

Lead mattes are, in the first instance, simply returned to the ore furnace in order to raise their percentage of copper to 12 or 14 per cent. They are then worked up by roasting and smelting together with a part of the ore charge, which serves the double object of extracting most of their lead and a good proportion of their silver while concentrating the copper, and securing an additional iron flux for the lead ore smelted.

Preparation.—Lead mattes are usually obtained in the form of cakes flat on the top and having the form of the slag pots into which they were tapped. These cones have to be broken up by hammers and passed through a stone-breaker and rolls as a preparation for roasting in reverberatory or other furnaces. When mattes are produced in large quantities in a liquid form, as is usually the case now, especially when internal or external forehearths, Livingstone separating pots, or Iles-Rhodes reverber-

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atories are employed, matte can be with advantage granulated like slag.

TABLE XXIV.—Analyses of Lead Mattes.

	Oker, Lower Harz.	Freiberg, Saxony.	Mechernich, Rhen. Prus.	Pribram, Bohemia.	Clausthal, Up. Harz.	Argo, near Denver, Colo.
Reference,	1.	2.	3.	4.	5.	6.
Pb,	5·09	20	8·01	11·16	12·44	26·60
Cu,	16·81	10	1·56	1·59	3·49	32·03
Fe,	30·53	40	61·00	41·31	48·64	9·50
Mn,	...	...	...	1·08	tr.	...
Ni and Co,	...	...	0·26	...	0·11	...
Zn,	16·35	1·5	...	11·55	4·31	4·29
As,	...	...	...	0·55	...	...
Sb,	...	...	0·28	0·93	0·13	...
Ag,	...	0·2	...	0·105	0·035	1·92
S,	18·38	...	25·19	22·23	25·65	21·70
CaO,	...	...	...	0·05	0·51	
MgO,	...	...	...	...	0·05	
Al_2O_3,	...	...	...	...	1·51	
K_2O,	...	...	...	...	0·13	
Na_2O,	...	...	...	...	0·10	3·58
SiO_2,	...	...	0·31	3·06	1·22	
SO_3,	...	...	...	...	tr.	
O and C,	...	...	3·49	4·79	2·03	
	...	...	...	...	...	100·00
Note.—Mode of combination of Fe in above—						
$AsFeS$,	...	...	64·13	37·70	56·84	6 %(?)
$AsFe_2O_4$,	...	...	12·67	12·60	7·37	...
$AsFe$,	...	...	11·01	9·51	7·13	...
$AsFe_2S_3$,	...	...	...	...	...	10 %(?)

References.—1, 2, and 3. Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 385. 4. *Oesterreichisches Jahrbuch*, vol. xxxix., p. 24. 5. Hampe, *Chemiker Zeitung*, 1882, vol. xvi., No. 28. 6. Pearce, *Trans. A. I. M. E.*, vol. xviii., p. 64.

At the *Arkansas Valley* (Leadville), and perhaps at some other large modern works, the molten matte tapped into hand pots is poured into the centre of a jet of water under pressure of 20 to 30 lbs. per square inch issuing from a flat fan-shaped nozzle (preferably of brass) about 3 inches by $\frac{1}{8}$ inch. Provided the matte be sufficiently hot, the water cold, and the pressure not too low, all the matte granules will pass an 8-mesh screen and can be

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roasted, while the pot shells which have to be roasted or returned should not exceed 5 to 8 per cent. of the whole. The advantages of this practice are obvious; the only disadvantage is the (comparatively little) trouble and expense required to collect the granules from suitable tanks and load them into cars for elevation to the roasters.

At the *Globe* Works Dr. Iles prefers to crush his matte, but adopts a very simple device as a preliminary preparation. The matte is tapped from the forehearths and reverberatory settlers into large cast-iron moulds on wheels, forming flat cakes, which weigh about a ton each. These are turned out on to the dump and, while still red-hot, sprayed by adjustable jets of water, under which treatment they break up, and each piece becomes fissured with innumerable joints so that the subsequent crushing is much facilitated.

Roasting of Lead Matte.—Lead mattes may be roasted (without crushing) in heaps, stalls, and kilns, and, after crushing, in reverberatory and mechanical furnaces. Formerly, the methods of roasting in lumps were almost invariably employed, as is still the case to some extent in Europe, but the losses are so great on this comparatively high-grade material that modern works employ almost exclusively hand or mechanical reverberatories. The reactions which take place in roasting matte are practically the same as those described in Chapter vi., except that they are simpler. With matte, however, the tendency to sinter is more marked than with ore (owing to its lower degree of fusibility), while the losses of precious metals are usually more considerable owing to the greater richness of the material.

Heap-Roasting.—All the objections to heap roasting of ores apply with even greater force to that of matte, while the result is usually less satisfactory.

At *Clausthal* (Harz) matte is roasted in heaps of 150 to 200 tons built on a bed of cordwood, with a second bed of brushwood and coal-slack between the largest lumps of matte ranged above it. The first burning lasts two to three months and yields about one-third as well-roasted product carrying about 6 per cent. sulphur, principally as sulphates. The remaining two-thirds require two or three more burnings in smaller heaps of 75 to 100 tons, built up as before, the well-roasted product being hand-picked and the residue passed on to another heap.

In *Utah* and other parts of the United States heap-roasting was commonly practised up to about seven years ago. The piles were usually made quite small, measuring 24 by 18 feet in the base and, say, 6 feet high, on a bed of light wood from 6 to 15 inches thick. They held about 80 tons each and burned from thirty to forty days. Fine matte was kept to spread over the heap and to check combustion in case the pile should get too hot, but in spite of this fusion or, rather, liquation of the lower part of the

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pile frequently took place. Terhune mentions* a case where the fused "bottoms" thus produced assayed twice as high in lead and silver as the original matte. He gives the cost of roasting down to an average of 6 per cent. sulphur, as $2.25 (9s. 4d.) per ton, made up of labour (breaking, transportation, building, and breaking down piles) $1.65 (6s. 10d.) and wood (one-seventh cord) 60 cents (2s. 6d.) per ton.

The only advantages of heap-roasting are cheapness and absence of expenditure on plant. Its principal disadvantages are:—(1) Slowness of roasting, which means locking up capital for months; (2) imperfection of roast, with the consequent necessity of rehandling and re-roasting a considerable part of the whole; (3) great losses of valuable metals through "dusting" and leaching out of silver and copper as sulphates.

Stall-roasting possesses the same disadvantages as heap-roasting, but in a less degree. Although some expenditure on plant is required, it is much less than in the case of furnace-roasting; while, compared with heap-roasting, the roast is quicker and more perfect, the losses by dusting and leaching are smaller, and the fumes, even if they are not utilised, can be rendered less obnoxious.

At *Przibram* (Bohemia) stalls† are used for roasting lead matte. They are built of slag-brick, and, besides the ordinary draught inwards through the loosely-built front walls, are provided with horizontal passages in the side walls, as shown in Fig. 32 (p. 82), which expedite the roasting and also bring it more under control. The well-roasted matte is about half the total charge of the stalls and contains 8 to 10 per cent. sulphur; all lumps containing more are re-roasted. The consumption of fuel is, of course, less than in heaps.

Kiln-roasting.—At *Freiberg* matte is roasted in the kilns already described in Chapter vi. as in use for roasting ore. At *Lautenthal* (Oberharz) kilns of the Freiberg type (*v.* Figs. 34, 35, p. 83) are employed, arranged in groups of six, and larger than the Freiberg kilns, being 13 feet 10 inches high, 7 feet 6½ inches wide, and 8 feet 4 inches deep. From the centre of each side rise saddle-shaped ridges dividing the roasted charge into four portions corresponding with the four doors, which facilitates the drawing. In order to prevent sintering, four parts of fresh matte are mixed with three parts of once roasted matte to form the charge, and the total output of each kiln is 2·2 tons per twenty-four hours, the roasted matte still, however, containing about 8 per cent. sulphur. The roast-gases contain by volume 5 to 6 per cent. SO_2, and the results obtained are better on this material than with the pyrites burners formerly in use, the product of which still contained 13 per cent. sulphur. These kilns are, of course, somewhat expensive to build and their out-

* *Trans. A.I.M.E.*, vol. xvi., p. 23. † Figured by Hofman, *op. cit.*, p. 257.

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put is not very great, but the recovery of the sulphurous gases is profitable, as there is a good market for sulphuric acid in the neighbourhood.

At *Mansfeld* argentiferous copper mattes containing 26 per cent. sulphur are roasted in 10 ton kilns, with cup and cone charging arrangement, and the gases are conducted to sulphuric acid chambers. The output of each kiln averages 1¼ tons of roasted matte per day, and each ton of matte produces 9 cwts. of chamber acid of 50° Baume. The roasted matte averages 10 per cent. sulphur, and is concentrated by smelting as usual. The sulphuric acid is mostly concentrated and sold for the manufacture of nitro-glycerine.

Matte Roasting in Reverberatory Furnaces.—Reverberatory furnaces used for matte roasting differ in no respect from those used in roasting ore, except that on account of the lower percentage of sulphur in the matte, it is not usually found advantageous to make them quite so long in proportion to their breadth. In Colorado, however, furnaces used for both ore and matte are of identical pattern, except that the sintering hearth often used for the former is never used for matte. The arrangement for discharging the roasted matte resembles that of the Przibram ore-roasting furnace shown in Figs. 36-38, p. 89 (Chapter vi.), there being one or two openings near the bridge (ordinarily closed with iron plates) through which the roasted matte is discharged into an iron truck in the vault below.

When siliceous lead ores poor in pyrites have to be sintered (which is not usually necessary) matte is sometimes mixed with them so as to afford the necessary iron flux, otherwise it is almost invariably roasted alone. Before roasting, it must be crushed so as to pass at least a four-mesh screen, and a six or eight mesh is decidedly preferable.

Matte charges are sometimes heavier than ore charges, but then the number worked off is so much less that the net daily output of each furnace is slightly lower than when it is working on ore. Usually, the furnace capacity on matte is slightly lower than on ore, the average time spent by each charge in the furnace is thirty to thirty-two hours; each furnace is worked by two men on each twelve-hour shift, and the consumption of coal is somewhat higher than when roasting ore, say 30 per cent. on the average.

Matte Roasting in Mechanical Furnaces.—Several of the mechanical furnaces have been tried on mattes and have given good results.

The **Brown Horse-Shoe Furnace*** is practically a Brown-Allen-O'Hara furnace bent into a circle, the inner diameter of which is 42 feet. One-fifth of the circle is cut out for a cooling and discharging space, and the ore is made to travel completely

* *v.* Peters, *Modern Copper Smelting*, 1895, p. 218.

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round the remaining four-fifths by means of the travelling table blades mounted on stirrer carriages. The average distance through which the particles of ore travel is 173 feet, which is much more than in most of the other mechanical furnaces, and the particles are more gradually raised to the required final temperature, so that the furnace would seem to be better adapted to the roasting of material high in lead, the tendency of which to sinter is very great.

One of these furnaces is at work at *Argentine* (Kas.), roasting lead-matte for the Hunt-Douglas wet process. The matte contains 10 to 20 per cent. Pb, 25 to 35 per cent. Cu, and is roasted at the rate of 18 tons per day, with a consumption of 3½ to 3¾ tons of slack, say 20 per cent. by weight. The calcined matte yields 87 to 92 per cent. of its copper in the soluble condition.

The **Bruckner Cylinder** has been successfully applied to the roasting of lead mattes at the *Germania* Works (Utah), the results being almost precisely similar to those with lead ores, except that, owing to the low melting point, somewhat greater care is requisite to prevent sintering, and that the daily capacity is somewhat lower, while the fuel consumption is a little higher.

The **Pearce Turret Furnace**, which has proved very successful in the roasting of coppery ores such as are commonly smelted at the Argo Works (for which ores indeed it was first designed), has been used for the roasting of lead matte both at the *Philadelphia* and *Colorado* Works (Pueblo); but it is not liked at either place, and at the latter it has been thrown out altogether.

The **Ropp Furnace** seems to be, as for ores, the most successful of the mechanical furnaces, but for both classes of material the vast majority of experienced lead smelters appear to prefer the old-fashioned hand furnaces, on account of the greater trustworthiness of the results, smaller fuel consumption, and less trouble from sintering.

Smelting of Roasted Matte.—The roasted first matte from lead blast furnaces is invariably used over again in the ore blast furnace as iron flux, being often kept to some one or more of the furnaces, the charge for which is made up to contain all the coppery ores available. Usually, however, with the larger matte production of modern American practice the roasted matte is used as iron flux on all the furnaces.

At the *Aurora* Works (Ills.) a first matte containing 7 to 15 per cent. Cu, 10 to 18 per cent. Pb, and 15 to 60 ozs. Ag per ton, is roasted and returned to the ore furnace until its copper contents are over 15 per cent., when it is roasted and concentrated by smelting with siliceous copper ores; the resulting second matte contains 10 to 15 per cent. Pb, 35 to 45 per cent. Cu, and 60 to 100 oz. Ag per ton, which is sold or worked up on a cupel hearth for gold-bearing bottoms and silver-bearing rich copper matte (*v.* Chapter xvii.).

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At the *Germania* Works (Utah) the first matte runs about 10 per cent. by weight of the charge, ranging from 8 to 10 per cent. Cu, and on an average 15 per cent. Pb; it is roasted and returned to the ore charge till it reaches 15 to 20 per cent. Cu. It is then roasted and concentrated in separate furnaces with siliceous copper ores, producing a second matte with about 40 per cent. of copper, which is sold to copper smelters.

It is noticeable that the charge for the concentration of matte requires more fuel than the ordinary ore charge; for example, 16 or 17 per cent. as against 13½ or 14 per cent. It is further worthy of note that the slag obtained by smelting roasted matte with siliceous ores, although low enough in silver, is usually higher in lead than an ordinary ore slag. Analysis invariably reveals the presence of Fe_2O_3 in these matte slags, and it has been suggested that the oxides of lead and iron probably exist in the slag mutually combined as a result of the reaction of litharge on magnetic iron oxide present in the roasted matte, the reaction being as follows:—

$$2Fe_3O_4 + 2PbO = Pb + 2Fe_2O_3 + PbO \,.\, Fe_2O_3.$$

In re-smelting roasted matte charges low in lead, "speiss" is very frequently produced. Sometimes it is a true speiss of the general formula, Fe_5As_2; sometimes, however, it is not an iron speiss at all, but is very rich in lead and copper, containing up to 30 per cent. of the former and 45 per cent. of the latter, besides being very rich in silver.

The further treatment of the enriched copper mattes obtained from lead works does not much differ from that of ordinary argentiferous mattes obtained from copper ores direct. Their treatment will, therefore, be most appropriately dealt with in a subsequent chapter, especially as it frequently takes place in distinct works under separate ownership and hundreds, or even thousands, of miles away.

Nickel and Cobalt in Matte.—The occurrence of nickel and cobalt in lead matte is unusual and worthy of special mention. At *Mine La Motte* (Mo.)* ores containing Ni and Co (about 2 of the former to 1 of the latter), the roasting and smelting of which has been already referred to, yield a first matte containing 3 to 3½ per cent. Ni and Co, 0·5 to 1 per cent. Cu, and 20 to 25 per cent. Pb. This is roasted in reverberatories and used as iron flux in the ore furnaces. According to Neill, it is necessary to leave 5 to 6 per cent. of sulphur in order to prevent slagging away Ni and Co. The second matte containing 5 to 6 per cent. Ni and Co, 1 to 2 per cent. Cu, and 20 to 30 per cent. Pb is roasted and smelted in a similar way except that in this case 7 to 9 per cent. sulphur is required to protect the nickel and cobalt.

Further concentration of the matte cannot be effected even in

* Neill, *Trans. A.I.M.E.*, vol. xiii., p. 634.

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a reverberatory, as the lead present appears to drive the Ni and Co into the slag. By taking advantage, however, of the well-known affinity of nickel for arsenic and smelting with mispickel or poor iron speiss. Neill found that a rich speiss of nickel and cobalt could be made, while the reduced lead carried most of the precious metals. The furnace used was 30 inches wide at the tuyeres, and 6 feet 6 inches high from tuyeres to charging door; it had a crucible 18 inches deep with syphon tap for the lead. The slag in this case contained only 0·16 to 0·32 per cent. Ni and Co, and 0·6 to 0·8 per cent. Pb; the impoverished matte, 3·25 per cent. Ni and Co, 8 per cent. Pb, and 7 per cent. Cu; while the rich nickel cobalt speiss contained 22·5 per cent. Ni and Co, 6·4 per cent. Pb, and 4·25 per cent. Cu: the silver and gold contents of the reduced lead paid for the whole cost of the operation.

3. SPEISS.

Composition.—The composition of lead speisses is given in Table XXV. from which it will be seen that they are chiefly arsenides of iron containing more or less sulphur, copper, nickel and cobalt, and lead, the last of which exists, however, chiefly as shots included mechanically. Guyard found also as much as 10 per cent. of metallic iron in the form of shots in speisses from Leadville furnaces, and the author can confirm the existence of metallic iron in some speisses from his own experience.*

Arsenides of iron corresponding to the formulæ Fe_2As_2, Fe_3As_2 and Fe_4As_2 can be prepared artificially; they are fusible at a high temperature, yielding white, fine-grained, brittle masses. The arsenides of formulæ Fe_5As_2 and Fe_6As_2 are those generally formed in furnaces smelting not only lead but (under certain circumstances) copper ores also. They are much more fusible than the arsenides lower in iron, and coarsely crystallise in large plates resembling "spiegel-eisen." Speisses still richer in iron corresponding with the formulæ Fe_8As_2, Fe_9As_2, and $Fe_{10}As_2$ are also occasionally formed, but, like those under Fe_5As_2, they are again fine grained, tough, and comparatively infusible, more resembling "sows" than true speisses, and probably in every case they contain more or less free iron.

Analyses of some speisses produced in lead furnaces are given in the following table, analyses of modern "hard head" from tin smelting works and of an old Roman speiss from Rio Tinto by

* According to Hofman (*Met. of Lead*, pp. 149 and 150) these speisses vary in composition from Fe_2As to Fe_6As. The same generally accurate author gives descriptions of the physical characters of speisses of different compositions, which unless he has, contrary to his usual practice, dropped back into the old notation (and, if so, the same slip is repeated in pp. 211 and 212) are incorrect. The mistake, curiously enough, is repeated by Furman in his article in the *School of Mines Quarterly*, vol. xiv., p. 137.

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the author being added for comparison. It is noteworthy that all speisses contain more gold than mattes produced at the same time, and that as regards silver and lead contents, the fine-grained varieties always carry more than those which are coarsely crystallised :—

TABLE XXV.—ANALYSES OF SPEISSES.

	Leadville, Colorado.	Leadville, Colorado.	Pueblo, Colorado	Eureka, Nevada.	Przibram, Bohemia.	Przibram, Bohemia.	"Hard-head," Corn-wall.	"Blan-quillo," Rio Tinto, Spain.
Reference,	1.	2.	3.	4.	5.	6.	7.	8.
Formula,	Fe_5As_2.	Fe_5As_2.	Fe_5As_2.	Fe_5As_2.	Fe_5As_2.	Fe_5As_2.	Fe_5As_2.	Fe_5As_2.
Ag, . .	0·0085	0·0301	0·014	0·0270	0·037	0·020	...	0·014
Au, . .	tr.	0·0009	...	0·0013	...	...	...	0·001
Pb, . .	1·4935	2·5030	0·690	2·1800	1·752	3·245	...	tr.
Cu, . .	0·3628	0·2536	5·060	1·0600	1·956	0·409	...	2·150
Fe, . .	60·5780	70·4780	59·420	57·0200	61·330	56·700	62·50	52·650
Mn, . .	...	...	...	...	...	...	...	0·010
Ni and Co.,	0·0876	0·0981	tr.	...	2·056 0·194	0·783	...	0·029
Zn, . .	tr.	tr.	tr.	0·0700	...	...	...	...
Mo, . .	0·2110	0·2125	...	2·3100	...	...	...	...
Sn, . .	...	...	...	...	...	...	17·25	...
Ti, . .	...	...	...	...	...	...	...	4·530
Ca, . .	...	...	...	...	0·500	0·535	...	...
Sb, . .	tr.	0·1450	tr.	0·1300	2·450	1·608	...	0·770
As, . .	31·4725	21·8003	31·170	32·9500	18·750	26·747	19·02	23·100
S, . .	5·8191	4·4625	2·800	3·3400	9·600	10·000	1·26	2·550
Al_2O_3, .	...	...	...	...	...	...	...	0·120
CaO, . .	...	...	...	0·3500	...	...	...	0·162
MgO, . .	...	...	...	...	...	...	...	0·127
SiO_2, . .	...	...	...	0·2300	...	...	...	0·081
Fe_3O_4, .	...	...	...	...	...	...	...	7·590
C, . .	...	...	...	...	...	...	...	3·130
N, . .	...	...	...	...	...	...	...	0·090
Loss, . .	...	...	...	...	...	...	...	2·896
								100·000

References.—1. Emmons, "Geol. and Min. Ind. of Leadville," *Mon.* xii., *U.S. Geol. Surv.*, p. 720. 2. *Id.* 3. Dewey, *Bull. No. 42 U.S. Nat. Museum*, p. 52. 4. Curtis, "Silver-Lead Deposits of Eureka," *Mon. VII. U.S. Geol. Surv.*, p. 160. 5. Balling, *Berg- u. Hüttenm. Zeitung*, 1867, p. 419. 6. *Id.* 7. Phillips, *Elements of Metallurgy*, 1891, p. 521. 8. Author, *Private notes.*

Treatment.—The speisses produced in lead works ordinarily contain 3 to 4 per cent. Pb, with from 10 to 16 ozs. silver, and 1 to 3 dwts. gold per ton. Their treatment, so as to extract all their

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silver, gold, and copper contents, offers some difficulties. In most works, when only a small quantity is occasionally produced, it is simply returned to the ore furnace. In some works, however, it is roasted in a reverberatory or in heaps of about 50 tons (badly roasted portions being returned to a new heap) and smelted as iron flux or together with roasted matte, when the greater part of its lead, gold, and silver contents are taken up by the work-lead, the copper going into the second matte, while the second speiss produced is poorer than the original, besides being much less in quantity, and simply goes to a fresh heap.

At Freiberg in 1860 a mixed matte and speiss containing 163 ozs. silver was smelted without roasting in small reverberatory furnaces together with quartz and heavy spar, the effect being equivalent to roasting off the sulphur according to Schweder's reaction. After skimming off the slag, metallic lead was added in equal quantity to the original speiss, the whole well rabbled, and the lead tapped off again with nearly all the silver contents of the original speiss, the cleaned speiss containing barely 7 ozs. per ton.

This process was improved at the Eureka Consolidated Works, Nevada, by Davies,* who employed an air blast for mixing the lead and speiss, and dispensed with the preliminary oxidising fusion. A small cylindrical converter, lined with firebrick, was employed, and holding at a charge 800 lbs. of cupola-melted speiss; to this was added from 20 to 25 per cent. of melted lead, and then a blast of air at about 17 ozs. pressure was passed through the mixture for several minutes by means of a ¼-inch pipe at the bottom of the converter. Some arsenic was burnt off, and some iron slagged, combining with the siliceous lining material; while most of the silver and gold contents were taken up by the lead. The converter was revolved by hand and emptied into a slag pot having a small taphole in the bottom, through which the still liquid lead was tapped after the speiss had set. The lead now contained 30 to 40 ozs. silver, and the speiss was poor enough to throw away. According to the results given by Davies, in the case of a speiss containing 9 to 10 ozs. silver, 85 per cent. of this metal and 89 per cent. of the gold were extracted with a loss of 5 to 8 per cent. of the lead employed.

The modern practice at Freiberg is to concentrate roasted speiss separately in a small Pilz furnace together with foul ore slag, lead residues poor in silver, old cupel hearths, and some fluorspar as flux for the latter. The product is a second speiss poor in silver, but rich in nickel and cobalt, which is subjected to a second similar concentration, and then goes to the smelting works to be worked up into metallic nickel, cobalt glass, and a lead which goes to the liquation furnace.

* *E. and M. J.*, June 20, 1888.

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At the *Germania* Works (Utah)* speiss is roasted (after crushing) in Bruckner cylinders, together with the ordinary sulphide ores, in any proportion up to 20 per cent., by which means nearly all of the arsenic is expelled as As_2S_3, which oxidises at once to As_2O_3 and SO_2. The mixture of roasted ore and speiss then goes to the ore furnaces, and requires much less flux than ore alone, owing to the ferric oxide into which the roasted speiss has been chiefly converted. This may be considered the best mode of dealing with speiss when it does not contain sufficient nickel and cobalt to justify the adoption of the Freiberg separate treatment.

4. SLAG.

Composition.—The constitution of lead slags has been fully discussed in Chapter vii., and their handling outside the furnace and separation from matte in the last chapter. Some analyses of lead slags have been collected in Table XXVI.

It is difficult to tabulate the analyses of some lead slags, on account of the doubt as to the mode of combination of Ba and of S. In slags comparatively low in zinc there can be no doubt that the S present is practically all combined with Fe, Pb, Cu, &c., in the condition of matte so finely disseminated as to be virtually in a state of solution, as shown by Mrázek.† This matte can be separated by fusion with borax, and contains practically all the valuable materials present in the slag. In non-barytic zinciferous slags most of the S may be considered as combined with Zn and Fe, though occasionally CaS may be present in slags from low furnaces. When much barium is present, part of it is always found as sulphide, BaS, which burns with the characteristic green flame when the slag is tapped; the remainder, in modern high pressure furnaces, usually exists as silicate, $BaSiO_3$, though in low furnaces, where reduction is not so powerful, most of it enters the slag unaltered as $BaSO_4$. Thus the exceptional slag produced in 1887 at the Goslar Smelting Works (No. 4, Table XXVI.) probably contained ZnS, BaS, and $BaSO_4$, as there calculated, though the analytical data quoted by Schnabel only show 23·4 per cent. BaO, 20·25 per cent. Zn, and 6·4 per cent. S. Many of the other slags in the table probably contain ZnS, though the figures have been quoted without recalculation. As regards the proportions of lead shown in the analyses, it should be borne in mind that slag samples for analysis are usually selected so as to be somewhat cleaner than the average, though of the same general composition.

* *Private notes.*

† *B. u. H. Jahrbuch*, 1866, vol. xvi., p. 392; quoted by Percy, *Met. of Lead*, pp. 407-409.

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TABLE XXVI.—Analyses of Lead Blast Furnace Slags.

	Muldener Hütte, Freiberg.	Mechernich, Rhen. Pruss.	Juliushütte bei Goslar, Lower Harz.	Idem. Exceptional.	Clausthal, Upper Harz.	Przibram Bohemia.	Mazarron, Spain.	Eureka, Nevada.	Tombstone, Arizona.	Mine La Motte, Mo.	Sunny Corner, N.S.W.	B. H. Block 14 Works, Port Adelaide.	Broken Hill Prop. Co., Broken Hill.
Reference,	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
SiO_2, . .	23·95	31·27	16·90	12·87	31·09	37·50	31·94	23·67	35·70	35·30	29·33	25	40·4
Al_2O_3, .	4·45	8·14	6·31	3·12	6·98	7·81	2·57	1·64	11·91	5·56	10·20	3	9·8
FeO, . .	44·41	35·61	35·05	20 64	40·64	28·37	35·42	58·32	12·09	35·90	40·30	29	13·3
MnO, . .	0·92	1·24	...	1·91	0·86	2·51	1·52	0·23	24·01	...	0·73	4	13·2
ZnO, . .	14·81	...	19·64	21·31	8·01	4·07	1·91	4·44	und.	...	3·20	16	3·4
CaO, . .	4·75	20·44	6·05	2·10	4·39	14·70	20·42	4·78	12·02	13·90	12·46	14	13·4
MgO, . .	0·54	1·18	0·60	0·72	0·05	1·11	0·78	1·27	2 80	9·27	...	...	1·4
K_2O, . .	} und.	und.	{ ...	...	0·58	} und.	{ 0·45	} und.	{ ...	...	...	...	...
Na_2O, .			{ ...	...	0 35		{ 0·34		{ ...	...	...	...	...
Pb, . .	2·66	1·04	1·17	0·77	1·70	0·41	1·88	3·26	1·64	0·52	1·15	und.	und.
Cu, . .	0·67	0·05	0·85	0·87	0·21	und.	...	0·86	...	...	0·41	...	...
BaO, . .	...	...	...	...	1·04	...	...	...	...	...	...	...	...
$BaSO_4$, .	und.	...	10·24	18·20	0·51	und.	...	...	...	...	...	...	...
BaS, . .	...	...	...	12·60	...	...	...	...	...	...	...	...	...
P_2O_5, . .	...	...	...	...	0·79	2·11	0·54	...	und.	...	...	...	...
Ag, . .	und.	und.	und.	...	0·002	0·00125	0·001	0·0018	0·006	und.	0·007	und.	...
Sb, . .	...	0·10	...	...	0·22	...	...	...	...	...	...	...	...
Ni and Co,	...	...	...	...	0·03	...	...	...	...	und.	...	...	...
Mo, . .	...	...	...	...	...	...	...	0·32	...	...	...	...	...
As, . .	...	...	...	...	...	...	...	0·25	und.	...	...	...	...
ZnS, . .	...	...	...	4·70	...	...	...	...	...	...	...	4	und.
S, . .	4·46	0·80	1·92	...	3·55	0·92	1·45	2·19	und.	und.	1·78	...	und.
	101·62	99·87	98·73	99·81	101·002	99·51125	99·221	101·2318	100·206	100·45	99·567	95	94·9

References.—1, 2, 3, 4. Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 348. 5. *E.M.J.*, Oct. 21, 1893. 6. Schnabel, *loc cit.* 7. Sanchez Massia, *Metallurgia del plomo*, Madrid, 1893. 8. Curtis, *Mon. VII. U.S. Geol. Survey*, 1889. 9. Church, *Trans. A.I.M.E.*, vol. xxiv., p. 561. 10. Kemp, *S.M.Q.*, vol. ix., p. 218. 11. *Private Notes*, 1887. 12. Average of 1896 *Private Notes*. 13. *Id.*

Note.—Some of the above analyses have been re-arranged by the author from the published data.

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It was pointed out by Pearce* that certain reverberatory slags made at Argo contained considerable proportions of magnetic material, which he assumed to be magnetite, and to be formed by the oxidising influence of the furnace gases upon the slag after the reducing effect of S and SO_2 had terminated. E. Keller has since shown† that much Fe_3O_4 (up to 18 per cent.) is frequently found in the slags produced by smelting roasted mattes in reverberatory furnaces, and smaller amounts are invariably present in matte slags produced in blast furnaces, the atmosphere of which is not sufficiently reducing to destroy this substance before it is taken up by the molten products. When the matte is of low grade and has a specific gravity not over 5·2 (the specific gravity of magnetite), the latter substance sinks into it in preference to going into the slag. When, however, a high grade copper or lead matte is being made, the specific gravity of which is over 5·3 or about that, the magnetite cannot enter the matte, and is carried away by the slag.

The losses of valuable metals in the slag take place in the following ways:—(1) Through fine visible shots of matte and occasionally even of metal; (2) through incomplete reduction of metallic oxides; and (3) through an almost infinitely fine dissemination of matte which is held by the slag, either in solution or in such intimate suspension of minute particles as practically to amount to a true solution. The loss in the first way is usually the most important, and can be almost completely eliminated by careful settling either inside or preferably outside the furnace, as has been already shown. The other two sources of loss can only be diminished by the use of an independent reverberatory settler in which a reducing flame is kept up, or by the precipitation by scrap iron in a suitable form of settler. Practically all the silver contained in a slag may be considered as existing in the condition of suspended matte, as is also most of the lead contained in modern clean slags from high pressure and high column furnaces. The slags from lower furnaces are, however, always richer in lead, especially when somewhat siliceous (as at Broken Hill), and in those cases part, if not most, of the lead probably exists as oxide.

Final Disposal of Slag.—This is frequently confined to wheeling the slag to the edge of a large and constantly growing heap from which it is sometimes loaded up again by railways and used as ballast. Other methods of finally disposing of liquid slag as obtained in large quantities, after its separation from matte by either of the devices already referred to, may be described under the following heads, viz.:—(1) Economical methods of simple removal; (2) methods by which the heat of

* *Trans. A.I.M.E.*, vol. xviii., p. 10. † *E. and M. J.*, Nov. 16, 1895.

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the molten slag is partly utilised; (3) methods by which the slag itself is utilised as a building material.

Methods of the First Class.—For economically disposing of a large output of molten slag where suitable conditions prevail, nothing is superior to the method of **slag granulation** in use for so many years at iron and copper blast furnaces, both in Europe and in the United States, and which has been recently employed at one or two American lead works. By the use of a powerful jet of water under considerable pressure, and a trough lined with sheet iron or, better, cast iron, a slope of ½ inch, or even as little as ¼ inch, to the foot is found sufficient to carry the slag to any required distance; though a slope of ¾ inch to the foot is far better as avoiding all risk of stoppage. At the *Hanauer* Works (Utah)* the trough is 150 feet long. 2 feet wide, and 6 inches deep inside the cast-iron bottom lining which is 1 inch thick. The "pitch" is only ¼ inch to the foot, and with a 13 feet head, the slag from four blast furnaces is carried to an elevator pit at the end of the trough, from which it is raised 40 feet by a belt elevator with sheet-iron buckets into a storage bin holding 100 tons, placed above the railroad track. The granulated slag passes a 4-mesh sieve, and affords great convenience for sampling and weighing so as to check the actual furnace losses; it is extensively used for ballast, but does not pack well under the sleepers.

A very ingenious method of automatically handling slag in a more advantageous condition for use as ballast is that devised by Page of the Omaha and Grant Works, Omaha.† About 75 feet from the furnace building is a circular pit, 35 feet diameter, at the edge of which revolves an annular disc composed of slightly dished cast-iron plates, 2 feet wide and 1¾ inches thick, which runs by means of rollers on a circular cast-iron submerged track resting on pillars all round the pit. A toothed wheel on the circumference of the disc engages with a pinion, by means of which it is revolved at the rate of one turn in five minutes. A constant stream of cold water enters the pit, and the hot water is run away just so fast as to keep the lower side of the cast-iron plates under water. As each slag pot is tapped on to the revolving plates the slag spreads out into a layer ¼ inch to 1 inch thick, and cools quickly, cracking up in so doing, so that at the end of the revolution a fixed plate of ½ inch steel against which the layer of slag impinges readily breaks it up into flat irregular pieces from ½ inch to 4 inches long and wide by ¼ inch to 1 inch thick, and forces it to pile itself on to a conveyor which takes it into bins from which the railroad trucks are loaded.

At the *Argentine* Works the slag from small slag pots is

* Terhune, *S. M. Q.*, vol. xv., p. 108.
† Braden, *Trans. A.I.M.E.*, vol. xxvi., p. 51.

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tipped into large trucks, into which strong pronged eyebolts are set before they are filled. When cold, a crane lifts the mass of slag by means of this eyebolt, and after it has been broken up by sledges it is run through a crusher and loaded direct into flat trucks belonging to the railway companies who gladly take it as ballast.

Methods of the Second Class.—Attempts have been made to utilise the waste heat of the molten slag for the purpose of heating the blast, and, as will be seen hereafter in the chapter on pyritic smelting, such attempts not only contain a germ of usefulness, but have already attained a fair measure of success as far as the matting furnace is concerned. The use of hot blast in lead smelting, however, is of doubtful advantage, and would probably result in enormously increasing the volatilisation losses, so that the field scarcely seems a promising one for experiment. Patents have been taken out for furnaces in which a mixture of air and petroleum vapour is to be heated in a sort of closed forehearth by the liquid matte and slag, but such a furnace would be wrong in principle, as well as unworkable in detail.

Attempts were made at Broken Hill by Howell and Ashcroft to utilise the heat of molten slag for raising steam. The apparatus consisted of a flat egg-ended steel-plate boiler containing vertical tubes of copper or wrought iron completely surrounded by water; the tubes were tapering, with the larger end downwards, and closed by cast-iron doors so arranged as to be easily opened and closed from one side by a system of lever handles. The boiler shell was fitted with a steam-dome safety valve, and other usual fittings, and sheet-iron bins lined with firebrick were provided at each end of the boiler to receive the "shells" from the pots, so as to help in keeping up the heat in the boiler. Both the "shells" and the cooled slag in the tubes were emptied into an iron truck running on a track beneath the boiler. The taper tubes were filled successively with slag by means of the ordinary slag pots, the first being emptied as soon as the last was filled. Unfortunately, it was found that the shells of slag formed in the tubes were such bad conductors of heat that the actual pressure of steam attained was only 20 to 30 lbs., an amount quite insufficient to be of any practical service under the local conditions prevailing at Broken Hill.

Methods of the Third Class.—Iron blast furnace slags have been utilised as building material both by casting them into slag bricks, and (as, for example, at Siegen) by granulating, grinding fine, calcining with limestone, and re-grinding for the manufacture of hydraulic cement. The slags in question, however, consist chiefly of an acid silicate of alumina and lime, and it is doubtful whether lead slags, which are much more basic and contain scarcely any alumina, could, under any circum-

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stances, be successfully utilised for the manufacture of cement, the results of experiments made up to the present being decidedly unfavourable.

Manufacture of Slag Brick.—To some extent the same objection is to be noted here, the best slags for slag-brick purposes being those containing upwards of 40 per cent. silica, which are not produced in lead smelting. Lead slags are generally too brittle and too much inclined to fissure on cooling, to make the best kind of building and paving brick, such as that produced at Mansfeld. Still, at most leadworks a few bricks are made for use in building ore-bins, foundations, dust chambers, &c., and there is no doubt that this could be extended with advantage. The manufacture of slag brick from reverberatory copper slag has been described by Dr. Peters,* and that from blast furnace slag at Mansfeld,† and in Montana,‡ is well described in two papers in the *School of Mines Quarterly*, to which reference should be made for details. According to the author's experience in making slag brick it is of the utmost importance that the slag should be as cool as possible before casting, and that the bricks should be cooled as slowly as possible by removing the moulds as soon as set and covering them several inches deep in sand. Dusting a little sand into the moulds as they are being filled also assists in the production of a slightly rough surface which is better for holding mortar than a smooth glassy one.

By proper annealing and toughening even paving tiles may be made from ferruginous blast furnace slags. Thus, at Santiago de Chili§ the slag is ladled from the slag pots into cast-iron moulds 6 inches square by 1 inch deep, each provided with a cover. After filling a lot of moulds they are covered and placed on a hearth, which has also a cover to anneal, a gentle heat being kept up so that the cooling operation may be slow. When the slag has cooled to a black heat, the moulds are lifted from the hearth and the tiles thrown into cold water to toughen them. The tiles are very hard and durable, and are worth, from £2 to £4 per 1000.

Another entirely distinct method of making slag bricks for building is that in use at the Lührmann furnaces, Osnabrück, Germany, where over 5,000,000 bricks have been made as follows‖:—The slag is granulated by a stream of water and then mixed with slaked lime in the proportion of 1 part of quicklime to 6 of granulated slag. The mixture is passed through a set of rolls and then through a mixing machine; the bricks are moulded in a machine which has a hopper filled by a labourer and which turns out the bricks automatically, subjecting each to

* *Modern Copper Smelting*, 7th Ed., 1895, p. 142.
† Egleston, *S. M. Q.*, vol. xii., pp. 112-117. ‡ *Ibid.*, p. 189.
§ Braden, *Trans. A. I. M. E.*, vol. xxvi., p. 52.
‖ *E. and M. J.*, Dec. 3, 1893.

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a great pressure by means of eccentrics. One pair of machines turns out 10,000 bricks per day, requiring 3 H.P. for the mixer and 8 H.P. for the moulder. The bricks are at first tender, and must be stacked carefully and protected from rain; but after six or twelve months exposure to air they become solid enough for building. The slag used at Osnabrück is, of course, the ordinary iron blast furnace slag, and it is very doubtful whether lead blast slags could be efficiently utilised in this way unless ground *very* fine.

Working up of Old Slags.—In many localities are found heaps of old slags resulting from the smelting of lead slags in very primitive hearths and other furnaces, and these are at the present time being profitably worked up.

At *Laurium*, Greece, two French companies have been for many years past smelting slags produced in the days of Xenophon; together with old slimes rich in silver from the ancient dressing operations, and lead concentrates from modern dressing works (the largest in Europe), treating the low grade ore bodies left behind in the mines. Between the two Companies no less than twenty-three water-jacketed furnaces, more or less of the Pilz type, but square, are at work, turning out, from charge mixtures averaging about 9 per cent. of lead, between 15,000 and 16,000 tons of base-bullion per annum. The following table gives the composition of some of the substances treated*:—

	Ag.	Pb.	SiO_2.	FeO.	Al_2O_3.	CaO.	Zn.
	Oz. p.t.	p. c.	p. c.	p. c.	p. c.	p. c	p. c.
Old slags (average), .	13·7	10·7	30·0	14·3	3·6	14·3	5·2
Old waste heaps, .	43·1	7·3	36·5	20·2	1·7	5·3	3·2
Old slimes, . . .	53·9	10·3	42·5	13·4	4·5	6·3	5·9
Old tailings, . .	98·2	3·6	15·0	17·4	...	25·0	6·5
Modern concentrates,.	104·5	32·2	15·7	8·1	...	17·7	7·2

The coke consumption is about 15 per cent. of the charge, and the slags thrown away contain only ·5 to 1 per cent. lead. Iron ore and limestone are used as flux, the former containing lead and silver, reaching occasionally as much as 6 per cent. of the former, and 65 ozs. of the latter.

At many other places in Europe and in South and Central America similar work is being done upon old slags.

Another method of cleaning zinciferous or other foul lead slags is by the use of pyritic copper ores. In a furnace at Leadville, 36 inches by 80 inches, one month's campaign described by Keller† consisted in smelting 3107 tons of slag with 5·3 ozs

* *Mineral Industry*, vol. ii., 1893, p. 410.
† Keller, *Trans. A.I.M.E.*, vol. xxi., p. 71.

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Ag per ton and 402 tons of pyritic copper ores, averaging 10 per cent. Cu and 11 ozs. Ag per ton. The matte produced was separated from the slag in an open settler forehearth, and averaged 20 per cent. Cu and 93·3 ozs. Ag, while the cleaned slag averaged under $\frac{3}{4}$ oz. Ag and $\frac{1}{2}$ per cent. Cu. The fuel consumption was 10 per cent., and the total cost per ton of material smelted only 6s. 3d.

OTHER FURNACE PRODUCTS.

Furnace Accretions.—These may be of two kinds—viz., hearth accretions or "sows" and the far commoner "wall accretions."

"**Sows**" may form on the hearth of a sump furnace, or above the lead bath in a furnace with crucible which is kept full. They are caused (1) by badly calculated charges; (2) by lack of fuel; and (3) by too slow a rate of smelting. The chief item in their composition is metallic iron, but they also contain lead, sulphur, arsenic, copper, nickel, and other substances, besides, occasionally, particles of coke, matte, speiss, &c., mechanically enclosed. When rich in lead and sulphur they are often comparatively rich in precious metals, and are then worth smelting down with siliceous ores on the hearth of a reverberatory furnace. When composed chiefly of metallic iron they are always poor in silver, and are rarely worth working, so that in such cases they are better thrown over the dump. In a large works with regular supplies of ores to draw upon and carefully calculated charges they are of very rare occurrence; perhaps only one or so in the course of a year. The composition of some "sows" from lead furnaces is given in Table XXVII.

"**Wall Accretions**" or "**Hangings.**"—These are chiefly composed of portions of half-smelted charge cemented together by sulphides with more or less oxides of zinc and lead. The way in which lead and zinc, together with some of their compounds, particularly the sulphides, are volatilised in the smelting zone of the furnace and become condensed in a partially oxidised condition in the upper portions from just above the jackets, more than half-way up to the feed floor, has been already described (Chapter ix.); as has also the method of removing them and smelting them out.

Some analyses of wall accretions are given in Table XXVII.

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TABLE XXVII.—Analyses of Furnace Accretions.

	Sows.		Wall Accretions.			
	Leadville.	Przibram.	Leadville.	Leadville.	Pueblo.	Globe Works, Denver. Average.
Reference,	1.	2.	3.	4.	5.	6.
Pb, . . .	18·793	20·140	47·491	21·317	1·48	24·06
PbO, . .	...	...	0·405	5·245	...	...
Zn, . . .	tr.	5·417	6·977	...	45·68	18·42
ZnO, . .	...	...	0 300	66·534	...	...
Fe, . . .	72·828	38·875	6·754	...	6·71	13·26
Fe_2O_3, . .	...	...	1·100	1·381	...	...
Mn, . . .	0·015	tr.	2·010	...	0·54	1·60
Cu, . . .	tr.	1·107	tr.	...	none	0·80
Ag, . . .	0·1149	0·160	0·0754	0·0944	0·0188	0·0909
Au, . . .	tr.	tr.	tr.	...	...	0·0060
As, . . .	5·083	2·389	0·039	...	none	...
As_2O_3, . .	...	..	...	0·071	...	...
Sb, . . .	tr.	0·735	tr.	...	tr.	...
Sb_2O_3, . .	...	...	...	0·056	...	...
Sn, . . .	...	...	...	...	...	...
Mo, . . .	0·161	...	...	...	...	...
Ni and Co,	0·045	tr.	...	...	...	...
P, . . .	0·109	...	0·945	...	...	...
C combined,	0·550	...	...	...	...	...
C graphitic,	0·750	...	...	...	...	...
SiO_2, . .	0·900	9·300	10·100	1·577	8·13	17·26
Al_2O_3, . .	...	...	1·672	0·328	...	...
CaO, . . .	...	0·780	5·361	0·200	6·20	3·30
MgO, . .	...	...	4·297	0·159	...	...
SO_3, . .	...	...	0·965	0·287	...	...
Cl and Br,	...	...	...	0·035	...	...
S, . . .	0·650	18·466	8·291	2·725	25 98	10·90
	...	...	...	...	...	...

References.—1, 3, and 4. Emmons, "Geology and Mining Industry of Leadville," *Mon. XII. U.S. Geol. Surv.*, p. 723 and 727. 2. Balling, *Berg- u. H. Zeitung*, 1867, p. 419. 5. Dewey, *Bull. No.* 42 *U.S. Nat. Museum*. 6. Iles, *S. M. Q.*, vol. xviii., pp. 20-21.

The subject of flue dust, its composition, collection, and treatment is dealt with in a separate chapter.

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CHAPTER XI.

BLAST FURNACE LEAD SMELTING—EXAMPLES.

It will be convenient to consider the chief centres of blast furnace smelting (outside the United States) in the following order:—Germany, Austria-Hungary, Spain, Australia. American practice having been fully described in the preceding chapters, it is not necessary to give detailed descriptions of their operations, besides which the author is not at liberty to publish details of the principal works which he has had the privilege of inspecting. A few comparative data will, nevertheless, be found in a subsequent Table.

GERMANY.

This country was the original home of blast furnace smelting. Labour and fuel being usually cheap as compared with new countries, greater attention is paid to the recovery from the ores treated of as much as possible of their valuable constituents, regardless of the complexity of the operations thus introduced; and occasionally without due regard to the expense and loss caused by too frequent handlings.

Smelting at Freiberg.—At *Freiberg* (Saxony) almost all kinds of ores are treated by a variety of processes which centre round the lead blast furnace, and which result in saving not only the lead, silver, gold, and copper, but also the greater part of the bismuth, zinc, arsenic, cobalt, nickel, and a considerable portion of the sulphur contained in the ores. The nature of these processes and their relationship to each other are well shown in a diagram figured in Prof. Sir W. C. Roberts-Austen's *Introduction*, p. 363, which represents the operations as now conducted, except that they have been lately simplified by bringing up the first matte to 30 per cent. copper matte at one operation; and so dispensing with the third Pilz furnace, except for the purpose of cleaning slag and of smelting speiss.*

The ores treated may be divided into five principal classes:—

1. Lead ores carrying from 15 to 80 per cent. lead and various amounts of silver, the average being 40 per cent. lead and 110 ozs. silver per ton.
2. Pyrites and copper ores containing from 1 to 10 per cent. copper besides iron, lead, zinc, silver, &c., all as sulphides.
3. Dry ores, that is, silver ores more or less siliceous, but poor in lead.

* *v.* also Percy, *Metallurgy of Silver*, pp. 544, *et seq.*; Schnabel, *Handbuch der Metallhüttenkunde*, p. 389, *et seq.*

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4. Zinc ores divided into (*a*) those containing less than 25 per cent. Zn; and (*b*) those containing upwards of this amount.
5. Arsenical ores containing various amounts of silver, and divided into "mispickel ores" and "mixed arsenical ores."

Of the above classes 1 and 3 almost entirely go direct to the roasting furnace mixture beds.

The ores of class 4 containing less than 25 per cent. zinc also go to the roast furnace beds, while those containing upwards of 25 per cent. are twice roasted, first in kilns and then in reverberatories, and then distilled for zinc by mixing them with charcoal, and heating in retorts in a regenerative gas furnace.

With regard to class 5, it is divided; ores poor in pyrites, which are chiefly arsenical, being roasted in a current of air to produce white arsenic; while the heavy mispickel and pyrites ores, containing sulphur and arsenic in the proportion of about two to one, or thereabouts, are distilled in closed retorts so as to yield realgar.

Such arsenical ores as may contain more than 25 per cent. sulphur and less than 10 per cent. As, together with the whole of the ores of class 2 and a few lots from classes 1 and 3 specially heavy in pyrites, as well as the residues from the realgar works, are roasted together to collect the sulphur for the manufacture of sulphuric acid. The lump ore is roasted in the kilns already referred to in Chapter vi., the fines in Gerstenhöfer and muffle furnaces. It should be noted that the sulphurous acid from the zinc ore roasters and from the arsenic glass works is also utilised in the sulphuric acid works. All these sulphurous gases contain more or less arsenic, which, by conducting the gases through a series of lead-lined dust-chambers before allowing them to enter the lead-chambers, separates out as As_2O_3; and this As_2O_3 is returned to the arsenic works to be worked up into the finest white arsenic glass.

The ores thus partially roasted in the kilns and Gerstenhöfer furnaces are by no means freed from their sulphur, but no more of it can be utilised with advantage for the manufacture of sulphuric acid; and so the residues go to the mixture beds of the long reverberatory roasters.

These mixture beds, therefore, contain (1) raw galenas carrying 26 to 79 per cent. lead, and 3 to 150 ozs. silver per ton; (2) raw siliceous lead and silver ores; (3) residues from the zinc works; (4) residues from the arsenic works; and (5) once roasted pyrites and coppery ores of all descriptions. Their average composition is —lead, 20 to 30 per cent.; zinc, under 10 per cent.; silica, 20 to 25 per cent.; sulphur, 20 per cent.; and silver, 30 to 50 ozs. per ton. The roasting is incomplete, 3 to 5 per cent. of sulphur being always left in the ore in order to collect the copper in a matte; at the end of the roasting proper the charge is "sintered" down in the sump at the firebridge end of the hearth.

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The furnace has been already figured and described in Chapter vi. (p. 91). The flue dust from these reverberatory roasters is very rich in arsenic, and is treated in the arsenic works.

The sinter-roasted ore is smelted in the Pilz furnace already figured and described in Chapter viii. (p. 140). The charge is composed of roasted ore mixed with about an equal weight of slag from the same furnace, which is used in order to clean the slags and also to assist in carrying away zinc, by which means campaigns are obtained of three or four years' duration. The daily capacity of each furnace is 30 to 35 tons of ore besides the slag, with a consumption of $5\frac{1}{2}$ tons of coke, equal to 16 per cent. of the ore or $8\frac{1}{2}$ per cent. on the whole charge; the number of men on each shift of twelve hours is usually five—namely, one feeder and one wheeler on the charging floor; and one smelter, one slag runner, and one odd man on the dump or lower floor. The furnace is worked as a sump furnace, lead and matte being tapped together (and speiss also when produced) into a movable exterior crucible or receiver on wheels, in which the various products separate into layers.

The work-lead produced carries from 200 up to 300 ozs. silver per ton and goes to the liquation and desilverising works. The slags formerly produced were rather more acid than monosilicates; with the increase of zinc contained in the ores, however, it has become necessary to run more basic slags, and those now made (*v.* Table XXVI.) are slightly more basic than monosilicates. They contain from 2 up to (occasionally) as much as 6 per cent. Pb, about $\frac{1}{2}$ per cent. Cu, 9 to 14 per cent. ZnO, and from 1 to 2 ozs. silver per ton. The speiss produced in ore smelting is set aside to be worked up with that produced in subsequent operations. The matte produced contains 15 to 25 per cent. Pb, 8 to 14 per cent. Cu, and 45 to 65 ozs. silver per ton. It is roasted first in kilns (the roast gases going to the sulphuric acid works) and then in Wellner stalls (*v.* Chap. vi.), being afterwards smelted together with the ore-slag, unless containing upwards of 12 per cent. Cu.

Slag Smelting.—The roasted matte still containing 5 to 8 per cent. of sulphur is smelted together with from one and a-half to twice its own weight of foul slag from the ore furnace, and a small quantity of lead skimmings and drosses from the tap pits, and residues from the liquation hearths. A charge of 300 kilos. ore-slag, 200 kilos. roasted matte, and 4 kilos. drosses is smelted in a furnace, precisely like the ore furnace, at the rate of 60 tons of mixture per twenty-four hours, with a coke consumption of only 35 kilos. per charge, or, say, 7 per cent. The products are:—

Second work-lead with from 130 to 200 ozs. silver per ton, which goes to the desilverisation works.

Second matte, "copper-lead-matte," or "slag-matte," with 25 to 30 per cent. copper, 5 to 8 per cent. Pb, and 25 to 50 ozs. silver

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per ton. This is brought up to "pimple metal" of 80 per cent. copper by one or two roastings and fusions; the further treatment of this material is described in Part II.

The slags produced in slag-smelting contain about 29 per cent. SiO_2, 37 per cent. FeO, 9 to 12 per cent. ZnO; they carry usually about 1½ per cent. Pb by wet assay, and ½ oz. silver per ton, and are clean enough to throw away. Occasionally, however, portions are richer, when they are re-smelted in a smaller Pilz furnace with the addition of about 1 per cent. of lead drosses. In this case the capacity of the furnace is 36 tons with a coke consumption of 11 per cent.

The speiss produced in slag-smelting is generally a good deal more than in ore-smelting. Both are laid aside together till sufficient has been collected for a campaign. It is then roasted and smelted in the small Pilz furnace, together with a large excess of foul ore-slag and smaller quantities of liquation residues, and cupel bottoms, with fluorspar as flux for the latter. An impure work lead is produced which carries most of the silver in the charge; a small quantity of matte which is added to the first or second matte; according to its richness in copper; and a second speiss. This is worked up by another roasting and smelting in the same furnace, yielding a third speiss with 16 ozs. silver, 15 to 20 per cent. nickel and cobalt, and about 20 per cent. copper, which is bought by the small works.

The methods of flue-dust collection employed at Freiberg are described in the next chapter; the total amount collected in 1893 was 9·7 per cent. of the weight of ore smelted, and this was treated by bricking and adding to the ore charge.

The series of operations employed at Freiberg is about as perfect as it can possibly be from a metallurgical point of view, except as regards the enormous amounts of foul slag and of lead fume produced in the ore-furnace. In this respect, economically as well as metallurgically, there is room for improvement by the substitution of long oblong furnaces of the American type, with syphon-tap lead wells, for the large round Pilz furnaces. The increased capacity thus obtained would involve some saving both of fuel and of labour, whilst the narrowed zone of fusion at the tuyere level would give a higher temperature there, a cleaner separation of matte from slag, and, therefore, a less quantity of foul slag to be re-smelted, as well as a very much lower volatilisation loss of lead and silver.

Mechernich.—The Mechernich ore consists of small spots of galena (and other lead ores) up to pea size, in certain beds of the Triassic (Bunter) sandstone, which are crushed and dressed to get out their metallic contents. The whole of the ore which reaches the smelting works, therefore, consists of "concentrates" of different degrees of fineness. These are roasted in the double hearth reverberatories referred to in Chapter vi.,

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and the composition of the slag roasted ore is given in Table XIX. (p. 125).

The roasted ore is smelted in small rectangular blast furnaces together with iron fluxes (puddle cinder and hæmatite ore) and limestone. Besides a work-lead of great purity containing only 6 ozs. silver per ton (which is afterwards recovered by the Parkes process) a small quantity of matte is formed which is roasted in stalls and added to the ore charge. The composition of the slag, matte, and work lead is given in Tables XXVI., XXIV., and XXIII. respectively.

Goslar (Lower Harz).—At the Sophienhütte and Juliushütte, ores from the celebrated Rammelsberg mine are treated. The heap roasting of these ores has been described in Chapter vii., and the leaching out of zinc sulphate is referred to in Chapter xiv. The composition of raw and roasted ores is given in Tables XII. (p. 75) and XIX. (p. 125).

The ores are deficient in silica for fluxing the bases, and being so high in zinc even after leaching of the fine portion require the addition of more iron in order to form the double subsilicate $ZnO.2FeO.SiO_2$. Both these conditions are satisfied by the use of basic ferruginous slags from the Oker copper works near by, containing 17 to 21 per cent. SiO_2, 66 to 70 per cent. FeO, and 1 to 2 per cent. Cu. To every 60 tons of roasted and leached fine ore is added 40 tons of unleached lump ore, 25 tons of ferruginous copper slag, and 20 or 30 tons of foul slag from the same process. The water tuyere furnace employed is that figured and described in Chapter viii.; it is blown by five 2-inch tuyeres, supplied with air under a pressure of 10 to 13 ozs., and puts through in twenty-four hours about 10 tons of ore (14 or 15 tons of charge), with a coke consumption of 15 per cent. of the weight of charge.

The products are work-lead with 32 ozs. silver per ton, matte containing all the copper and a small part of the lead and zinc, clean slag which is thrown away, and foul slag (2 per cent. of the whole) containing 5 to 7 per cent. lead as shots of matte. The composition of the clean slag is given in Table XXVI. (p. 210). A flue dust rich in zinc is also produced, the composition of which is given in Table XXXI. (p. 238); this is worked up by leaching with sulphuric acid and crystallising out the white vitriol. The matte is once roasted in heaps and re-smelted together with the foul slags from the ore smelting, and fresh copper slag from Oker, yielding a small quantity of enriched matte, work-lead, and a clean slag with only $\frac{1}{2}$ to $\frac{3}{4}$ per cent. lead which is thrown away.

The slags produced at these works are of a most unusual composition. Schnabel quotes * the following analysis of an exceptional slag produced in 1897, viz.:—SiO_2 12·87, Al_2O_3 3·12,

* *Handbuch der Metallhüttenkunde*, vol. i., p. 389.

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BaO 23·40, CaO 2·10, MgO 0·72, FeO 20·64, Zn 20·25, Pb 0·77, Cu 0·87, Mn 1·48, S 6·40 = 92·62. It is not easy to see the mode of combination of the above slag, but probably the Mn was as MnO, and the Zn partly as ZnO, partly ZnS, while the Ba was partly as BaS, but chiefly as $BaSO_4$.

Clausthal (Upper Harz).—At Clausthal and Lautenthal is to be seen at work the only surviving example of the old precipitation process by which raw lead ores in a fine condition are charged into a blast furnace together with iron ores and slags. By the use of a high furnace and a small quantity of low pressure blast, the temperature before the tuyeres is kept high, while the rate of smelting remains low; sufficient metallic iron is reduced to partially decompose the sulphide of lead, producing metallic lead and an iron matte which takes up the undecomposed lead sulphide. It has been already noted that this reaction generally comes into play more or less in the ordinary blast furnace reduction process when sulphide lead ores are present in the charge, but at Clausthal it is the sole reaction relied upon. By this slow rate of smelting the consumption of fuel is very high, and the labour cost per ton smelted is also much greater than in the roast and reduction process; while, allowing for the subsequent roasting of the matte, it can hardly be said that the saving of roasting on the ore is a sufficient offset to these disadvantages.

Both circular and oblong furnaces are employed in the precipitation process in the Upper Harz, the latter being a modification of the Raschette furnace, and the former from the Pilz, with a good many modifications. The circular furnace used has been already figured in Chapter viii.; the pressure of blast under which it works is from 7 to 8 ozs.

The average composition of rich dressed Clausthal ore is given in Table XII. (p. 75), somewhat poorer ores containing only 50 per cent. lead, and up to 30 per cent. of insoluble residue. The average ore mixture contains, for every 100 tons of this ore, about 200 tons of other material made up somewhat as follows:—50 tons roasted ore matte, 50 tons matte slag (from the next operation), 80 tons ore slag from the same furnace, 5 tons of leady residues and drosses, and 15 tons of burnt pyrites, tap cinder, and similar iron fluxing materials. Formerly, the quantity of ferriferous slags used was much larger, but now reliance is chiefly placed on roasted matte as a means of supplying the iron required for combining with the sulphur of the ore.

The total quantity of the above mixture passed through a round furnace, of the dimensions shown in Fig. 56 (p. 143), with a blast pressure of 6 to 8 ozs., is about 10½ to 11 tons, corresponding to only 3½ tons of ore. The consumption of coke is about 13 per cent. on the whole charge or 40 per cent. on the ore, and three men are required on each twelve-hour shift—viz, one smelter,

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one feeder, and one slag runner. The slag flows continuously, lead and matte being tapped together from time to time, the matte cake being lifted from the still melted lead as soon as set. For every 60 tons of lead set free about 65 tons of matte are produced. The composition of lead, matte, and slag are given respectively in Tables XXVIII. and XXIX.

The working up of the matte consists of a series of alternate roastings and smeltings. The roasting in heaps at Clausthal and in kilns at Lautenthal has been already referred to in Chapter x. The smelting takes place in small square masonry furnaces of antique pattern, with one or two tuyeres in the back. The roasted matte is smelted together with 140 per cent. of ore slag, and the coke consumption is 20 per cent. of the weight of matte or 8 to 9 per cent. of the weight of charge. The small quantity of work-lead produced is richer in silver than that produced direct from the ore, containing 70 ozs. silver per ton as against about 48 ozs. A second roasting and smelting produces a third lead and enriched matte; while a third roasting and re-smelting gives no more lead, but only an impure black copper with 30 per cent. of lead. The two (sometimes three) following roastings and smeltings give further quantities of purer black copper, but the matte continues about the same in percentage—viz., between 57 and 60 per cent. Cu.

The following table shows the weights of lead, matte and black copper obtained at each successive concentration smelting, beginning with 1000 tons of ore (to which are added in the ore furnace 500 tons of roasted matte and 1500 tons of fluxes and slags):—

	Tons Lead.	Tons Matte.	Tons Black Copper.
Ore smelting produces, . . .	600	650	...
1st matte smelting produces, . .	52	150	...
2nd ,, ,, ,, . .	9	40	...
3rd ,, ,, ,, . .	...	18·4	4
4th ,, ,, ,, . .	...	7·3	4·6
5th ,, ,, ,, . .	...	4·4	1·4
6th ,, ,, ,, . .	often	omitted.	
Final products, . .	661	4·4	10·0

The following tables, compiled from data quoted by Schnabel,* give the analyses of slag and matte obtained from each concentration smelting, the original matte and ore slag being added for comparison:—

* *Op. cit.*, pp. 406 to 413.

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TABLE XXVIII.—Matte Analyses (Clausthal).

	1st or Ore Matte.	2nd Matte.	3rd Matte.	4th Matte.	5th Matte.	6th Matte.
Pb, . . .	12·44	8·01	13·00	9·06	6·32	3·88
Cu, . . .	3·49	12·29	35·72	42·30	58·10	59·86
Fe, . . .	48·69	45·62	21·88	19·98	11·01	12·24
Zn, . . .	4·31	3·36	2·23	1·59	0·96	0·75
Ag, . . .	0·035	0·035	0·08	0·075	0·06	0·035
S, . . .	25·65	21·80	19·49	17·89	20·15	20·78
	94·615	91·115	92·40	90·895	96·60	97·545

TABLE XXIX.—Slag Analyses (Clausthal).

	1st or Ore Slag.	1st Matte Slag.	2nd Matte Slag.	3rd Matte Slag.	4th Matte Slag.	5th Matte Slag.
SiO_2, . .	31·09	24·91	27·21	17·43	17·06	18·97
Al_2O_3, . .	6·98	4·50	5·85	5·87	5·36	6·47
FeO, . .	40·64	51·85	54·56	62·14	65·08	61·84
MnO, . .	0·86	0·75	1·07	0·49	0·56	0·50
NiO + CoO, .	0·03	0·13	0·06	0·27	0·34	0·54
ZnO, . .	8·01	6·56	6·24	4·30	2·55	2·90
BaO, . .	1·04	...	...	...	...	...
CaO, . .	4·39	4·25	5·46	2·00	2·32	2·27
MgO, . .	0·05	0·38	0·52	0·39	0·24	0·47
K_2O, . .	0·58	0·51	0·64	0·57	0·63	0·77
Na_2O, . .	0·35	0·33	0·31	0·33	0·41	0·53
Pb, . . .	1·70	1·55	2·25	1·47	1·02	0·92
Cu, . . .	0·21	0·90	1·39	1·90	1·88	1·58
Ag, . . .	0·002	0·0022	0·0012	0·0015	undet.	undet.
Sb, . . .	0·22	0·20	0·08	0·09	0·34	0·20
$BaSO_4$, . .	0·51	0·30	1·11	tr.	none.	none.
P_2O_5, . .	0·79	0·69	0·85	0·43	0·45	0·47
S, . . .	3·55	3·86	2·34	1·47	1·02	0·92
	101·02	101·4922	99·9512	99·1515	99·26	99·35

Comparing the above series of operations with the ordinary modern processes by which lead matte, in only two operations, is converted into a rich copper-silver matte and an impure silver lead, it is evident that there is unnecessary complication here, even allowing for the fact that only a small part of the original matte treated has to undergo the concentrations from No. 2 onward. While at Clausthal there may possibly be something to be said for the retention of the precipitation process in

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preference to roasting the ore direct, there can be no valid reason why the treatment of matte (up to the point where silver extraction commences) should not be cut down to two or, at most, three concentrations instead of five, as above. The last of the three concentrations could be made to yield "pimple regulus," as at Freiberg, or a "black copper," if it were preferred to adhere to the Oker process of silver extraction. Altogether, the series of operations seems too complicated, and will probably ere long give place to more modern and direct methods.

AUSTRIA-HUNGARY.

Przibram (Bohemia).—This is the largest individual metallurgical centre of the Austro-Hungarian empire. An analysis of the ore treated is given in Table XII. The roasting furnaces, twelve in number, are figured and described in Chapter vii. An average sample of the ore as roasted contains 34 per cent. lead and 0·260 per cent. (85 ozs. per ton) silver, while, after roasting, the sulphur contents do not exceed 1 per cent., the proportion of copper being so small that there is no need to leave sulphur in the roasted ore to protect it from being carried away in slag.

The roasted ore is mixed with fluxes (tap-cinder, roasted pyrites, and limestone) in the proportion of 37 tons fluxes to 100 tons of ore. It is smelted in seven round water-block furnaces (described in Chapter ix.) with eight 2½-inch tuyeres supplied with air at 13 ozs. pressure. In twenty-four hours 22 tons of ore are put through, or a total of 31 tons of charge, the fuel consumption being 16·4 per cent. coke and ¾ per cent. (1½ bushels per ton) of charcoal.

The work-lead produced contains about 150 ozs. silver per ton. The matte is very small in quantity, and is returned to the ore furnace after roasting in the stalls described in Chapter x. The clean slags containing under 1½ per cent. lead and ¾ oz. silver per ton are thrown away, a large part being, however, utilised for the manufacture of slag brick. Foul slags containing more than the above-mentioned proportions of lead and silver are returned to the furnaces. Analyses of work-lead, matte, and slag are given in Tables XXIII., XXIV., and XXVI. respectively.

SPAIN.

Of late years several large establishments have been erected in this country to work fusible lead ores together with old slags, the furnaces and the work generally following the German system of large round furnaces, with re-treatment of slags in the same furnace.

Mazzarron, near Cartagena.—At this establishment, which turns out over 20,000 tons of lead annually, three large round

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furnaces are kept running to treat 80,000 tons of ore. They are of the Pilz type, two of them being 6 feet in diameter at the tuyeres, 9 feet at the throat, 18 feet high from tuyeres to feed floor, and having eight 2-inch tuyeres supplied with air under a pressure of 6 ozs. The remaining furnace is oval, 10 feet by 6 feet at the tuyeres, and 29 feet high, with sixteen tuyeres. Sea water is used for the jackets, and the blast is supplied by four No. 3 Root blowers.

The mixture treated is as follows:—Roasted lead ores, 100 tons; irony old slags, 12 to 15 tons; iron ores, 25 to 35 tons; limestone, 20 to 25 tons; slag returned, 40 to 50 tons—total, 210 tons. Of this mixture the two small furnaces smelt about 110 tons each, equal to 50 to 55 tons of ore per day; the large furnace about 140 tons, equal to 65 to 70 tons of ore daily. The furnaces are charged as usual for large round furnaces, coke being thrown to the centre and ore spread round the sides. They are worked as sump furnaces and tapped four times a day, yielding 6 to 8 tons of lead at each tapping, besides a small quantity of matte. The slag runs continuously, and a large proportion of it, containing under 1½ per cent. lead, is clean enough to throw away. Its analysis is given in Table XXVI.

The condensing flues are 3½ kilometres in length, and the fume produced assays on an average over 50 per cent. lead. Analyses of it are given in Table XXXI. It is treated by bricking with lime, sand, and a little fine galena ore and adding to the ore charge on the last hearth of the roasting furnace, where it is sintered down with the ore.

AUSTRALIA.

At the **Broken Hill Works of the Broken Hill Proprietary Company**, siliceous and ferruginous carbonate ores (containing some galena) are smelted on a very large scale in fifteen of the so-called 80-ton furnaces similar to that shown in Figs. 65 and 66, but on a smaller scale, being only 112 inches by 60 inches. The quantity of ore treated per day is about 48 tons per furnace, exclusive of lime and returns. The average yield of the 120,484 tons smelted during 1896 was 7·76 per cent. Pb and 21·5 ozs. Ag, the 9357 tons work-lead produced thus averaging 207 ozs. per ton. Besides the lead, 1406 tons of matte were produced (or 1·16 per cent. on the ore) carrying 13 per cent. Cu and 114 ozs. Ag per ton, all of which were shipped to the refinery at Port Pirie to be worked up. The limestone flux used (92 per cent. $CaCO_3$) costs 14s. per ton, and the coke (9 per cent. ash) 57s. 6d. to 60s. per ton, delivered at the works. Owing to the high cost of fuel and flux, a siliceous slag is run which is supposed to increase the furnace capacity, at the expense, however, of much higher furnace losses.

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The slag produced is run off from the furnace continuously through the matte-separator, or internal forehearth already described (Chap. viii., p. 171), into the large double-pot trucks, also referred to, which are drawn by horses to the dump. The lead produced being small in amount is only tapped from the lead well about once, or at most twice, in a shift. A hemispherical cast-iron ladle with spout attached is so arranged as to revolve upon a pillar in front of the furnace; the end of the spout thus traverses in succession a row of reversible moulds placed upon a frame in front of the furnace, so as to cast the lead direct from the well without any ladling or drossing. As the refinery belongs to the same company, and the dross has ultimately to be worked up into copper matte, no inconvenience results from this economical practice.

The furnaces are fed through "open tops," and the column of charge in the furnace is kept 5 feet below the feed floor, leaving the "downtake" free; each plant of furnaces (nine in the north plant, six in the south) is provided with a separate flue and a stack, 180 feet high by 10 feet diameter, of sheet iron lined with one thickness of brick. The flue space provided is, however, utterly inadequate to condense the enormous amount of fume produced, and the volumes of dark grey smoke issuing from the stacks prove the losses of lead to be unusually heavy for a large smelting plant. In criticising this heavy loss it should be borne in mind that the *net* value of lead in flue dust at Broken Hill, allowing for treatment and realisation charges, is very much smaller than at American or European smelting works, and, in fact, lead is about the cheapest thing that Broken Hill metallurgists have to handle.

Each plant of furnaces is run from a single blast main in the usual American style, so that no details of construction call for special notice, except the water tuyeres already referred to. Further data as to the work done are given in Table XXX.

At the **Broken Hill Block 14 Smelting Works** (Port Adelaide, S.A.) four furnaces are in blast, treating an ore charge of unique composition. About three-fourths of the ore treated, or two-fifths of the total charge, including fluxes, is composed of roasted concentrates and slimes from the concentrating plant of the Company's mines at Broken Hill. The former contain 55 to 60 per cent. Pb, 25 to 30 ozs. Ag, and 8 to 10 per cent. Zn; the latter, 30 to 35 per cent. Pb, 20 to 25 ozs. Ag, and 15 to 20 per cent. Zn.

These concentrates and slimes are mixed in any convenient proportions according to the stocks on hand, and roasted in the three-hearth reverberatories described in Chapter vi. No attempt is made to roast below 7 to 10 per cent. S, as it is found that, by using a large volume of blast so as to keep the furnace gases oxidising, or at least not distinctly reducing, the reactions

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so well-known in connection with reverberatory smelting come into play, and reduce the lead just as well as if the roast had been complete and reduction were effected as usual by means of CO and glowing carbon. The ore is, therefore, rushed through the roasters at the rate of nine charges in twenty-four hours (an unusual procedure for such material), and the temperature on the last hearth is just high enough to bring about incipient softening and to form lumps. There are thirteen of these roasters in operation, all of uniform type; there is no appreciable volatilisation loss; and the flue dust formed is trifling in amount. Further details about the roasting process are given in Table XIII.

The remainder of the ore treated consists of siliceous and ferruginous carbonates similar to those treated by the Proprietary Company, but only about half as rich in silver. The fluxes used are barren iron ore with 15 per cent. silica, costing 10s. 6d. per ton; and limestone (96 per cent. $CaCO_3$), costing 6s. 3d. per ton; the fuel being English coke (7 per cent. ash), costing 29s. to 33s. per ton, all delivered at the works. The large furnaces employed have been described and figured in Chapter viii., but their manipulation is attended with some special difficulties on account of the high zinc contents. The "hangings" gave great trouble until it was discovered that "drawing in" the furnace from immediately above the jackets to the bottom of the down-take by only 6 inches or so, all round the furnace, thus giving a slight overhang to the brickwork, was of very great efficacy in preventing their growth. The very large amount of fume given off caused trouble to the feeders when the ordinary open tops were used. This could have been got over by using a stronger chimney draught at the expense, however, of less condensation and higher losses. Recently, a large ventilating hood in the roof has been provided at a considerable height over each furnace, and connection is made with this by means of a sheet-iron chamber provided with large feed doors at each side, and running on wheels so as to be easily run back for barring the furnace.

Each furnace is run by its own independent blower, a plan which, as already seen, possesses many advantages, especially when the ores are not very docile. The tuyeres of these furnaces being almost absolutely air-tight, and the loss by "slip" on Baker or Root blowers running rather slowly under a low pressure being small, it is easy to calculate the ratio between the quantity of air passing through the furnace and the fuel consumed.*

* For instance, the "100-ton" or smallest sized furnace, is run with 112 revolutions per minute of a No. 5 Baker blower, which delivers at a low pressure about 25 cubic feet per revolution. One cubic foot of air at 60° F., and at mean sea level pressure, weighs 0·0765 lb., therefore, the weight of air entering the furnace is *218 lbs. per minute*. The furnace smelts, on an

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Each furnace is provided with two distinct syphon taps on the same side, terminating in very small lead wells. These are tapped alternately at short intervals into small cooling pots, where the lead is allowed to cool, and is very carefully "drossed" before ladling into the usual series of reversible moulds hung upon frames, the abundant dross (chiefly PbS) being cast into two or three bars which are returned to the furnace.

The column of charge is run quite exceptionally low, usually about 8 feet below the feed floor, making the stock line only about 7 feet above the centre of the tuyeres. The down-takes of all four furnaces lead to a single flue 7 feet wide, 12 feet high, and 400 feet long, in which 6 per cent. of the total weight of ore smelted is collected. The stack at the end is 10 feet in diameter and 120 feet high. Slag taps * and spouts are provided at each end of the furnaces and are used alternately, so as to keep both ends as far as possible under equal conditions. The slag is partly run out in small pots and used for extensions to the works, which are built upon a reclaimed foreshore, and partly in large single pot trucks like those described in Chapter viii., but with a taphole provided for running out the molten interior on the Devereux principle. In either case, the whole of the slag-shells made (amounting to some 20 per cent. of the total slag) are returned to the furnace. The composition of the slag is given in Table XXVI.; it contains a large amount of ZnS which burns and smokes so much at the taphole and in the pots that a separate ventilating chimney, 5 feet in diameter, has to be run up over each slag tap to take off the fumes. With the exception of this inconvenience, and of the necessity for keeping a very close watch upon the running of the furnace, regular descent of charges, breaking up of incipient "scaffolds," and good condition of the tuyeres, very little difficulty is caused by the high zinc contents of the charge. The slag produced is hot and

average, 76 tons of charge per day, and at 11 per cent. this is equivalent to 8·36 tons of coke consumed per day, which at 90 per cent. carbon = 7·5 tons carbon = 700 lbs. carbon per hour. Now 700 lbs. carbon will require different quantities of oxygen, according to whether the burning is to CO (as generally assumed) or to CO_2:—

700 lbs. Carbon require :—	Burning to CO.	Burning to CO_2.
Oxygen, ...	933 lbs.	1,867 lbs.
Air containing 23 per cent. O, . .	4,058 ,,	8,116 ,,
Equal per minute, ...	67·6 ,,	135·3 ,,

Neglecting, therefore, slip and leakage at the blower and connections, which at this low pressure cannot amount to more than 15 or 20 per cent., we see that the quantity of air passing through this furnace is about three times that required for burning the fuel to CO, and 50 per cent. more than is required for burning to CO_2. The atmosphere inside the furnace, therefore, considered as a whole, cannot possibly have any reducing action; but must be, to a considerable extent, oxidising in its effects.

* i.e., matte-separating taps, or "internal forehearths."

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runs very thin; unlike the more siliceous slags, however, which pass through a plastic stage, it sets suddenly on cooling, and becomes quite hard and strong while still at a bright red heat.

For anything like good work the composition of these slags, containing 14 to 15 per cent. of metallic zinc, must be kept within very narrow limits for both silica and lime, the limits for the former lying between 23½ and 26 per cent., and for the latter 12 to 16 per cent. If the slag contains less than 10 per cent. lime, it carries away matte in suspension and the losses are increased; if there is more than 16 per cent. lime, the slag becomes mushy and gives rise to bad, irregular smelting. If the silica falls to 21 or 22 per cent., the losses of lead and silver in the slag are at once largely increased; if, on the other hand, it rises above 26 per cent., the lead loss increases rapidly without a corresponding increase in the silver loss, which, in fact, is generally lower on account of the larger amount of matte made. The non-formation of matte when smelting an ore charge containing 6 to 8 per cent. of sulphur and producing a normal slag, and its immediate appearance as soon as the silica contents of the slag rise above the normal limit without any change in other conditions, is one of the most remarkable facts brought out by the novel work of Mr. T. J. Greenway on these zinc ores. There seems to be no doubt whatever about the fact, which has been repeatedly observed whenever the ratio of silica to iron in the charge increased either by accident or design. The explanation is by no means obvious, but a clue is afforded by the fact that the matte so formed is not the ordinary iron matte but one very high in lead and zinc, and containing only a small percentage of iron. Further, it has been noticed that a rise in silica is always accompanied by a rise in lead, even though the silver contents of the slag remain low. But for this fact it might be argued that the formation of matte upon the slag becoming more siliceous was due entirely to more perfect separation of heavy metallic sulphides dissolved in the slag through the decreased specific gravity caused by the added silica; and, no doubt, some action of the kind does take place, as such siliceous slags are found to be somewhat more free from sulphur than those ordinarily made. The increased amount of lead in the slag, however, indicates that some other influence is simultaneously at work, and the explanation would seem to be somewhat as follows:—

The atmosphere in the upper part of the furnace being oxidising or, at all events, non-reducing, a portion of metallic lead is reduced there by direct reaction between the oxidised and unaltered portions of the charge. In practice, somewhat more than one half of the original sulphur contents of the ore is eliminated during roasting, and it may be reckoned that the

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bulk of the lead is converted into oxide and sulphate, while most of the zinc remains as sulphide. The large excess of lead oxide in the "carbonate" ores combines with the silica in the same ores to form silicates, which (together with the unaltered zinc sulphide of the roasted ore, some lead sulphide, and the fluxes) remain without change, except the elimination of CO_2 from carbonates, until reaching the zone of fusion where they react upon each other.

When the furnace is running as usual and producing a normal slag, the reactions which take place may perhaps be approximately represented by the following hypothetical equation :—

$$\overbrace{2(3PbO \cdot 4SiO_2)}^{\text{Ore.}}_{1724} + 4ZnS + PbS + \overbrace{4Fe_2O_3 + 4CaO}^{\text{Fluxes.}} + \overbrace{2O_2}^{\text{Blast.}} = \underbrace{4(2FeO \cdot SiO_2) + 2(2CaO \cdot SiO_2) + 2(2ZnO \cdot SiO_2)}_{\text{Slag (85 per cent. of total)} = 25\frac{1}{2} \text{ per cent. } SiO_2} + 5SO_2 + 6Pb$$

Supposing now the ore and iron flux simultaneously become more siliceous (as frequently happens) without any other change in their composition or in the furnace manipulation. Matte is made, as already seen, and the loss of lead in the slag at once goes up. The altered reaction may, perhaps, be shown by the following hypothetical equation :—

$$\overbrace{(5PbO \cdot 9SiO_2)}^{\text{Ore.}}_{1660} + 4ZnS + PbS + \overbrace{3Fe_2O_3 + SiO_2 + 4CaO}^{\text{Fluxes.}} + \overbrace{O_2}^{\text{Blast.}} = \underbrace{3(2FeO \cdot SiO_2) + 4(CaO \cdot SiO_2) + PbO \cdot 3ZnO \cdot 3SiO_2}_{\text{Slag (85 per cent. of total)} = 29\frac{1}{2} \text{ per cent. } SiO_2} + \underbrace{PbS \cdot ZnS}_{\text{Matte.}} + 3SO_2 + 3Pb.$$

The above equations must not be taken as representing definite equivalents, but they may serve to explain the nature of the change which probably takes place when the charge becomes more siliceous.

The peculiar practice at these works, though well suited to the abnormal conditions to meet which it has been adopted (including in particular the exceedingly high percentage of zinc), is by no means to be recommended for such conditions as ordinarily prevail in "custom" lead smelting works in other parts of the world.

Various other details are given in Table XXX., No. 3.

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TABLE XXX.—Examples of Lead Blast Furnace Smelting.

	Aurora, Ills. 1895.	Broken Hill Prop. Coy., Broken Hill. 1896.	Broken Hill Block 14 Coy., Port Adelaide. 1896.	Philadelphia S. & R. Works, Pueblo, Colo. 1897.	Pennsylvania Smelting Works, Utah. 1896.	Germania Works, Salt Lake City. 1897.
Reference,	1.	2.	3.	4.	5.	6.
Number of furnaces in blast,	8	15	4	8	4	4
Dimensions at tuyeres, ins.,	60 × 96	60 × 112	60 × 160	42 × 120	45 × 140	45 × 140
Height from tuyeres to feed floor, ft.,	16	15′ 2″	14′ 8″	17½	20	20
Downtake overhead or under floor,	...	underneath	underneath	underneath	overhead	overhead
Number and diameter of tuyeres,	8 of 3½″	11 of 3″	18 of 3½″	12 of 3½″	14 of 3½″	14 of 3½″
Description of tuyeres,	Projecting 12″	Projecting 8″	Projecting	Plain flush	Plain flush	Plain flush
Average blast pressure employed, ozs.,	...	11 to 13	12 to 14	28	36 to 40	36 to 40
Weight of charge—Carbonate ores, lbs.,	...	125	250	...	400	...
Roasted ,, ,,	...	...	850	...	200	...
Siliceous ,, ,,	...	425	400 to 500	...	300	...
Iron flux ,, ,,	...	175		...	600	About 300
Limestone, ,,	...	275	200 to 100	...		
Slag, ,,	...	10 % extra	200 to 250	...	250	About 100
Total weight, ,,	...	1000	2000	...	1750	1500
Weight of coke per charge, ,,	...	125	220	...	200	...
Percentage of coke on charge,	10½ to 12½	12½	11	13½	11½	12 to 13
Total wt. of charge smelted per 24 hrs., tons,	90 to 100	70	95 to 110	100	130 to 160	160 to 180
Percentage of lead on charge,	10 to 30	9 to 15	20 to 30	9 to 11	18 to 20	11
Weight of bullion produced per 24 hrs., tons,	7 to 20	...	15 to 20	...	...	15 to 17
,, matte ,, ,, ,,	2 to 5	...	none	...	5 to 6	14 to 16

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TABLE XXX. (*continued*).

	Aurora, Ills. 1895.	Broken Hill Prop. Coy., Broken Hill. 1896.	Broken Hill Block 14 Coy., Port Adelaide. 1896.	Philadelphia S. & R. Works, Pueblo, Colo. 1897.	Pennsylvania Smelting Works, Utah. 1896.	Germania Works, Salt Lake City. 1897.
Reference, ...	1.	2.	3.	4.	5.	6.
Composition of matte—Lead, . per cent.,	10 to 18	20 to 30	...	14	About 12	12 to 15
Copper, . ,,	7 to 20	6 to 15	...	8	About 10	8 to 10
Silver, ozs. per ton,	15 to 60	150 to 160	...	...	40	130 to 200
Composition of slag—SiO_2, . . per cent.,	33 to 40	40·4	23·5 to 26	...	33 to 36	37
FeO and MnO, ,,	28 to 35	26·5	32 to 34	...	30 to 33	30
CaO and MgO, ,,	10 to 22	14·8	13 to 15	...	18 to 23	22
Al_2O_3 . . ,,	2 to 10	9·8	2 to 4	...	3 to 4	5 to 6
ZnO, . . ,,	3 to 10	5·4	15 to 20	...	3 to 5	2 to 3
Pb, . . ,,	under 1	2½ to 3	2½ to 3½	0 8	½ to ⅝	1½ dry
Ag, . ozs. per ton,	under 1	2	1 to 1	0·6	0·6 to 0·8	·55 to ·65
Percentage weight of flue-dust saved, . .	3	5	6	1½	2 to 3	2 to 2½
Value of flue dust—Lead, . . per cent.,	11 to 25	...	25 to 60	...	20 to 25	...
Silver, . ozs. per ton,	13 to 50	...	...	...	20 to 25	...
Cost of coke per ton of 2240 lbs., . . .	...	57/6 to 60/	29/ to 33/	...	...	...
Method of separating slag from matte, .	"internal fore-hearth" = matte tap,	"internal fore-hearth" = matte tap,	tapped pots all shells saved.	overflow pots shells saved,	...	external forehearth,
Area of furnace at tuyeres, . . sq. ft.,	24	33·5	44·4	36	43·75	43·75
Total area of tuyeres, . . . sq. in.,	77	105·8	173·2	115·45	134·7	134·7
Tuyere ratio, ...	3·21	3·15	3·9	3·20	3·08	3·08
Hearth efficiency (average), ...	3·7 to 4·2	2·09	2·1 to 2·3	2·77	3·0 to 3·7	3·6 to 4·1
Tuyere efficiency, ...	1·15 to 1·31	0·663	0·54 to 0·59	0·86	0·97 to 1·20	1·20 to 1·33

1. *Private communication*, E. S. Eurich. 2, 3, 4, 5, and 6. *Private notes*, 1896-1897.

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AMERICA.

The author not being at liberty to give detailed descriptions of specified works visited has selected as typical examples of American practice the data given in columns Nos. 1, 4, 5, and 6 of Table XXX. The comparative figures there given will, it is hoped, be found useful, and particular attention should be drawn to the way in which the figures for "hearth efficiency" and "tuyere efficiency" rise in proportion to increased blast pressure.

The following examples of unusual conditions may be quoted:—

Tombstone, Arizona.*—Here, during the years 1883-1887, concentrates from the tailings of pan amalgamation mills containing 50 per cent. Pb, 50 ozs. Ag, and about ½ oz. gold per ton were smelted together with argentiferous manganese and siliceous ores in a round water jacketed cupola, after "bricking" with the finest slime from the settling pits, which itself contained 8 to 10 per cent. lead and a little silver. The total quantity treated was about 40,000 tons, the average lead contents on the charge being only 6·7 per cent. by dry assay, and the base bullion produced averaging 329 ozs. Ag. per ton; yet the losses in slags averaged only 1·64 per cent. lead and 1·8 ozs. silver per ton, though running much higher when the lead on the charge ran down to only 4½ per cent. It was necessary to charge back the bullion produced in order to keep sufficient flow through the furnace. It appeared that good work could be done when the lead produced was not less than 7½ per cent. of the total weight of the fused furnace products. The slags made were very fluid (owing to the manganese present, which at times ran as high as 43 per cent.) their average composition is given in Table XXVI. The fuel consumption was high—viz., 20 per cent.—owing, no doubt, in part to the oxidising influence of the free oxygen in the manganese ore. No difficulty was experienced except that the perfect fluidity of the basic manganese slag permitted all impurities to settle out and form crusts on the lead. This tendency was increased by the absence of sulphur to form a matte, and by a very small quantity of arsenic which formed a heavy infusible speiss with reduced iron and small quantities of copper, nickel, and antimony present. The total cost of smelting, including limestone flux, was 39s. 11d. per ton of ore.

At **Casapalca, Peru,** 14,000 feet above sea level and 2000 feet above timber line, rich lead and silver ores are smelted in water jacket furnaces with imported English coke, costing $40 per ton. The ores consist of—(1) Lump galena with 45 per cent. Pb and 50 ozs. Ag per ton; (2) jig concentrates with 158 ozs. silver per ton; and (3) Vanner concentrates with 209 ozs. silver per ton. All the concentrates contain 6 to 12 per cent. of lead and

* *v.* Church, *Trans. A.I.M.E.*, vol. xv., p. 601; vol. xxiv., p. 559.

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3 to 5 per cent. copper. The ores, mixed in the proportion of two parts lump galena to one part concentrates, are charged in 1 ton charges into a single-hearth reverberatory for roasting and slagging. Each charge takes six hours to work, the fuel being 300 lbs. of soft coal (local, costing $16 per ton) and 250 lbs. of dried llama dung. The slagged ore contains Pb 34·5 per cent., Cu 9·3 per cent., Ag 0·34 per cent., SiO_2 17·2 per cent., Fe_2O_3 22·5 per cent., CaO 6 per cent., S 6·5 per cent.—total, 96·34 per cent.

The slagged ore is broken into fist-sized pieces and smelted in a 36-inch round American water jacket. The average charge is 18,000 lbs. slagged ore, 500 lbs. of ancient slags with 45 per cent. Pb and 2 to 5 ozs. silver per ton, 300 to 500 lbs. of oxidised ores, 1000 lbs. of bog iron ore, 1500 lbs. of limestone, and 1500 lbs. of fou slags with 8 to 12 per cent. Pb. The products are work-lead with 235 ozs. silver per ton, and copper matte with 27 to 50 per cent. Cu, 7 to 61 per cent. Pb, and 38 to 150 ozs. silver per ton. The slags average SiO_2 37 per cent., FeO 45·2 per cent, CaO 8·6 per cent., Pb 3·4 per cent.; when not containing over 6 per cent. lead they are considered "clean" and are thrown away, as it would not pay to resmelt them on account of the high cost of fuel. The coke consumption is 14 to 17 per cent. of the charge, which is small enough considering the very high altitude.

CHAPTER XII.

FLUE-DUST—ITS COMPOSITION, COLLECTION, AND TREATMENT.*

1. COMPOSITION.

THE term "flue-dust" is commonly applied to a product which, collected very often in a single series of apparatus, is in reality composed of a mixture in varying proportions of two distinct classes of material. The first is merely fine ore-dust carried over mechanically by the draught; the other, more properly called lead-fume, being a mixture of sulphides, sulphates, and oxides of lead with some zinc, arsenious acid, and other substances,

* Consult Hering, *Die Verdichtung des Hüttenrauches*, Stuttgart, 1888; also Hofman, *Metallurgy of Lead*, 1893, pp. 281, *et seq.*; and Iles, *S.M.Q.*, vol. xvii., pp. 97, *et seq.*

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volatilised in the hottest part of the furnace, and subsequently solidified on cooling into an infinitesimally fine dust. The individual particles are so fine that it would be almost impossible to collect them but for their mutual attraction, which causes them to form flaky or feathery aggregates somewhat as snow crystals combine to form snowflakes. The flue-dust collected nearest the furnace contains most of the particles of ore mechanically carried over, while that further away approximates to the composition of a true fume.

The flue-dust from blast furnaces run with a cold top is always dark in colour, owing to the presence of particles of fuel in the dust chambers near the furnace, and to the presence of large quantities of volatilised PbS at a greater distance along the flue. The marked difference in composition between mere chamber dust and true fume is well exemplified by the analyses of the products of the Lone Elm hearth furnace given in Chapter v., p. 73, and the difference is quite as marked in the case of blast furnaces. The flue-dust from roasting furnaces contains little or no ore and fuel, approximating more to the character of a fume, while the fume from furnaces in which the ore is fused or slagged is naturally much richer both in lead and silver than when the ore is plain roasted.

The composition of various samples of flue-dust is given in Table XXXI. It will be noticed that a considerable proportion of PbS exists in most of the samples. The volatility of PbS at moderate temperatures, much below its fusing point has been already referred to in Chapter ii., and hence it is to be supposed that all the lead existing as PbS in flue-dust was volatilised as such, while that existing as PbO was probably volatilised as metal in the lower portion of the furnace. When, as frequently happens, the deposited fume catches fire and burns in the flue on account of some furnace being barred down or blown out, the residual matter consisting of sulphates and oxides, acquires a white or grey colour. This is always the case with fume from reverberatory furnaces.

Careful testing of the flue-dust from different parts of a condensing system brings out the fact that the ratio of silver to lead diminishes with increased distance from the furnace. This is only what might be expected from the less volatility of silver compounds. Thus, at Ems the silver in the flue-dust and fume diminishes gradually from nearly 5 ozs. down to 1 oz. per ton. Flue-dust is always relatively poorer in silver than the ore from which it was derived, for the same reason; and fume-lead (obtained as its name implies chiefly from the true fume or finer portion of flue-dust) is harder and more impure as well as poorer in silver than ore lead.

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TABLE XXXI.—Flue-Dust Analyses.

	Freiberg, Saxony.	Upper Harz.	Lower Harz (Goslar).	Ems, Rhen. Prussia.	Pontgibaud, France.	Cartagena, Spain (crude).	Cartagena, Spain (calcined).	Wyandotte, Mich.	Pueblo, Colo.	Reverberatory, Bagillt, Flintshire.	Reverberatory, Bagillt, Flintshire.	Reverberatory, Sheffield.
Reference,	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Pb,	...	34·8	...	67·04	...	...	...	...	...	...	...	...
PbO,	27·90	18·0	20·26	...	60·15	...	23·65	19·91	37·65	46·54	62·26	44·80
$PbSiO_4$,	...	2·9	...	...	...	...	...	...	...	...	...	...
PbS,	...	...	...	...	...	71·13	57·31	...	...	...	...	...
Zn,	...	1·0	...	...	...	...	...	...	...	4·87	1·05	...
ZnO,	49·50	1·5	28·90	4·22	10·50	4·17	...	0·09	5·32	...	...	...
CuO,	...	...	0·72	tr.	...	...	...	...	tr.	1·60	1·60	4·80
CdO,	...	...	...	...	...	...	...	...	...	...	...	...
Bi_2O_3,	...	...	...	...	...	...	...	...	...	...	...	1·52
Sb_2O_3,	...	4·0	...	0·31	4·30	1·89	4·40	...	...	...	...	3·03
As_2O_3,	2·13		...	0·16	3·25	...	0·54	...	...	...	...	
Ag,	...	...	0·07	0·003	...	...	...	0·286	0·04	...	...	...
Fe,	...	1·4	...	...	...	...	...	...	...	...	...	...
Fe_2O_3,	...	...	...	1·00	1·30	8·54	11·84	14·43	24·98	4·16	3·00	tr.
Al_2O_3,	...	4·5	...		...	...	...		1·31	...	...	10·00
NiO,	...	...	...	...	...	...	...	0·08	...	...	...	...
CoO,	...	...	...	...	...	...	...	0·09	...	...	...	...
CaO,	7·00	...	0·45	0·61	...	3·64	0·92	8·74	5·26	6·07	3·77	...
MgO,	...	...	...	...	...	0·34	0·17	3·66	...	...	...	...
SiO_2,	...	12·3	18·14	...	...	...	...	16·11	8·63	10·12	1·97	9·00
S,	...	7·8	5·43	5·42	...	6·70	...	...	2·53	...	...	...
SO_3,	13·00	2·8	...	14·07	18·60	...	0·90	9·30	1·61	26·51	25·78	28·81
H_2O,	...	...	9·58	...	...	...	...	1·28	11·20	...	...	...
CO_2,	...	...		5·80	1·60	3·17	...	19·23				
C,	...	2·5										
	99·53	93·5	...	98·633	99·70	99·58	99·73	93·206	98·53	99·87	99·43	101·96

References.—1. Hering, *Die Verdichtung des Hüttenrauches*, 1888. 2. Balling, *Metallhüttenkunde*, p. 87. 3. Schnabel, *op. cit.*, p. 389. 4. Egleston, *Trans. A.I.M.E.*, vol. xi., p. 397. 6 and 7. Sanchez Massia, *Metalurgia del Plomo*, Madrid, 1893, p. 293. 8. Curtis, *Trans. A.I.M.E.*, vol. ii., p. 95. 9. Dewey, *Bull. 42 U.S. Nat. Mus.*, p. 53. 10 and 11. Percy, *Metallurgy of Lead*. 12. French, *E.M.J.*, January 17, 1880.

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2. FLUE-DUST COLLECTION OR CONDENSATION.

The two varieties of flue dust—viz., true-dust and lead-fume—differ greatly as regards the difficulty of collecting them. The former only requires sufficient reduction in the velocity of the air current in order to settle out almost completely, even without thorough cooling, and this reduction in velocity is best secured by enlarging the diameter of the flue, and especially by constructing large dust or settling chambers. The floating particles of true fume, however, are so minute that, even after a thorough cooling (without which no condensation is possible), mere ordinary *settling* has but little effect upon them. A better means of condensation is to increase the length of the flue, and alter frequently the direction of the motion by means of baffle walls, so as to increase the number of contacts with the sides of the flue, to which a certain proportion of the floating particles adhere, and from which they fall to the floor.

It is found, however, that both of these means are comparatively inefficient for condensing true lead-fume, and accordingly at all the older lead works the length of the flues was continually increased, with the result that each successive addition yielded sufficient lead to more than pay interest on the capital expended in its construction. In this way, for example, the flues at Freiberg have grown till they now attain the enormous length of 5 miles, the sectional area being for the most part 40 square feet; again, at Mazarron, Spain, the flues are 2 miles long, and are being continually added to. The methods adopted for the condensation of flue-dust may be considered as belonging to the two separate stages of *cooling* and *collection*.

Cooling.—The first essential in condensing lead-fume is that the gases shall be thoroughly *cooled*, not, however, on account of any trifling amount of lead which may possibly remain in the condition of vapour, for the vapour tension of lead or its compounds, even at the boiling point of water, is quite imperceptible.

According to the experiments of Iles,* the average temperature of the gases escaping from a modern lead blast furnace in good work is about 214° F., the maximum registered being 335°, when the accretions had reached a considerable thickness. When the heat is allowed to creep up, however, and the furnace has a "hot top," the temperature may be very much higher.

Thorough cooling is necessary, chiefly because minute hot particles repel instead of attracting each other, and, therefore, until the gases are brought down to a temperature below that of boiling water, no collection of the particles into flaky masses can take place. The temperature of furnace gases from lead

* *S. M. Q.*, vol. xvii., p. 19.

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blast furnaces is, according to the above figures, not commonly high, and the cooling is, therefore, readily affected; but with gases from roasting furnaces and from reverberatories, which on entering the flue are still almost red hot, special means of cooling are essential.

Air Cooling.—A common method of air cooling is by means of a sheet-iron flue, as shown in Figs. 100 and 101. The former represents the flue in use at *Richmond* (Nevada), which was 800 feet long, and shows the mode of suspension to a wooden trestle.

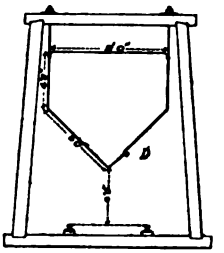

Fig. 100.—Flue.

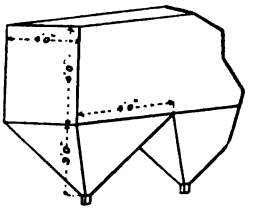

Fig. 101.—Flue.

The sliding doors, D, were 2 feet apart. A better arrangement is that shown in Fig. 101, where the flue-dust collects in the hopper-shaped portions which end in short square pipes closed by sliding doors, and which can be conveniently emptied into a closed truck by means of a movable length of pipe. This flue can be suspended by means of short trestles underneath the upper body, leaving the hopper parts hanging free. An arrangement of hoppers which is easier to make is that in use at *Ems*, but the hoppers are wedge formed, instead of pyramidal, and are not nearly so easy to clean. All sheet-iron flues should be kept well painted with some form of asbestos or "silico-graphite" paint.

Another air-cooling arrangement is that in use at the *Grant* Works, Denver, where, owing to want of space underground, flues and chambers have been built of hollow terra-cotta tiles, through which a current of air is made to circulate by means of a separate chimney.

Water Cooling.—Simple air cooling requires very long flues, and, therefore, many attempts have been made to utilise water for accelerating the rate of cooling. When applied internally, water also assists in condensing the dust, but this plan has many disadvantages, as will be seen under the head of *Wet condensation*. The external use of water for condensation is exemplified by the *Hagen* appliance in use at Freiberg. This is made of sheet lead; it is suspended like an ordinary sulphuric acid

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chamber, and cooled by a succession of shallow leaden tanks attached respectively to the roof and floor, and connected by elliptical sheet lead pipes burnt on to the sides of the flue and to each other. Water circulates alternately up and down through this series of tanks and pipes; the appliance is said to be very efficient in cooling the gases, though too costly for ordinary use.

Collection.—The collection of flue-dust, of course, begins before the gases have been properly cooled, and further cooling takes place during the collection. This further cooling is important, because the dust-laden gases are repelled by a surface which is warmer, and attracted by one which is at a lower temperature than their own. The preliminary partial cooling is, however, essential.

After cooling, the most important requisites for condensation are:—(1) To reduce the velocity of the air current; and (2) to expose as large a condensation surface as possible to the gases. Simple increase in the length of the flue fulfils to some extent the second condition, but not the first; large settling chambers fulfil the first condition, but not the second. Of the two requisites, the second is of very much greater importance than the first. It is found that in a horizontally partitioned flue very much more flue-dust is deposited in the upper than in the lower half in a given time; also that the point of maximum velocity is on the centre line of the flue at about seven-tenths of the total height from the bottom. At the bottom the forward velocity is very slight, or there may even be a slight eddying or return current, yet not so much is deposited here as on the top, where the velocity is much greater. In an ordinary flue without horizontal partitions the deposit on the bottom constantly accumulates, because the flue-dust caught on the top and sides falls from time to time in masses of greater or less size and remains there.

Increase of surface, however, without previous cooling has but little effect. Aitken has shown * that a hot surface *repels* floating particles, especially if moist; whereas a surface which is slightly cooler than the floating particles *attracts* them. Increasing the surface acts also in another way—viz., by increasing the friction of the current of gases, by which their velocity is considerably reduced within an inch or two of the surface, and the tendency of the particles to settle out can better come into play.

Construction of Flues and Settling Chambers.†—Both flues and settling, or dust, chambers are commonly built of brick, tied together by means of iron rods to avoid leakage. The parts near the furnaces are always built of firebrick, or of sheet iron as already described; but, after thorough cooling of

* *Proc. Roy. Soc. Edin.*, vol. xxxii., p. 239.

† Sometimes called "Sedimentation chambers."

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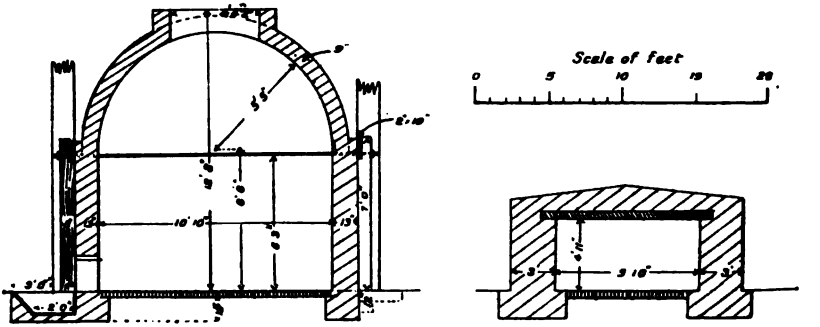
the gases and condensation of most of their contained moisture, ordinary brick or stone may be used for the remaining portions. Substantial construction is essential if the flues are to stand for any time, and thus a properly designed system becomes very expensive. Two very good forms of flue are shown in Figs. 102 and 103. The former* represents the flue of the Montana Smelting Company at one of the manholes 50 feet apart; the cleaning doors and pits shown in this figure occur on alternate sides at intervals of 9 feet 4 inches, and the method of bracing with wooden posts set into a masonry foot and tie-rods through the springing of the arch is plainly shown. Fig. 103 is a section



Figs. 102 and 103.—Flue.

of the new flues at the *Ems* Smelting Works. Arched flues were formerly used here, like those in Fig. 105, but they were found to crack a good deal, and flues of the form shown in the figure in which a course of iron rails across the side walls supports brickwork have, to a great extent, replaced them.

Baffle walls in the flues, forcing the gases to take a tortuous course and largely extending the surface, are found to greatly increase the amount of flue-dust collected, though somewhat diminishing the draught. It is best to run up these baffle walls from alternate sides so as to cover about one-half of the sectional area of a large flue, and to supplement them, as at *Aurora* and other places, by 2-feet walls built up from the floor at intervals, so as to form pockets, which prevent the dust from drifting along the flue or being again caught up by the current.

Where *brick* cannot be obtained, *stone* may be used for building flues, but they are not then so strong, and much more mortar is required. Occasionally, in countries where water for mortar mixing is scarce, flues have been excavated in the solid rock, and lined with a plaster of cement mortar, or with a lining of brick set edgeways. This method of construction, however, will rarely

* Borrowed from Hofman, *op. cit.*, p. 289.

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be much cheaper than that of ordinary flues above ground, and it possesses the great disadvantages of not being readily accessible for cleaning purposes, without shutting down the furnaces, and of not favouring any cooling of the gases. In old established works, however, flues have frequently to be built entirely underground on account of want of space.

Of late years the **Monier** system of construction * has been a good deal employed for the construction of flues and dust chambers, for which purpose its lightness and the thinness of the walls render it specially suitable. A flue on this principle (a network of coarse iron wire imbedded in cement concrete) was erected in 1890 by the Victor Friedrichshütte (Tarnowitz, Up. Silesia), 1640 feet long, 6 feet 7 inches wide, and 9 feet 10 inches high, which has given satisfactory results. A group of condensing chambers on this system was built in 1893 at Freiberg, as an addition to the flues from the arsenic and zinc works. It consists of six parallel flues, each 100 feet long, 10 feet 4 inches wide, and 10 feet 10 inches high, giving a total extra length of 686 feet of flue, with 2086 cubic metres capacity.

The lattice work is composed of vertical and horizontal wires, $\frac{9}{32}$ inch apart, the wires being $\frac{9}{32}$ inch and $\frac{3}{16}$ inch diameter respectively. The concrete is composed of one part cement, three parts quartz in fragments, about $\frac{1}{2}$ inch diameter, and two parts quartz tailings from the dressing floors. The walls are built 20 inches thick, with the network in the middle; they are painted on the outside with coal tar and on the inside with a silicate paint. The cost was £1330, as against £1500 which it would have cost in light brickwork, and £2500 in sheet lead properly supported.

Similar flues have been constructed at other places in Europe and America, † and are found to answer very well, except that the difference of temperature between the outside and inside surfaces, and especially the difference between night and day temperature, causes the cement to crack. This can, however, be remedied by building the flue in short sections only, 6 feet long, with a $\frac{1}{2}$-inch space between, and covering with thin flat strips of iron so as to form a rough expansion joint.

Methods of Increasing Surface.—In addition to baffle walls, the principal methods of increasing surface are the following :—

1. **Cowper Flues.**—The principle upon which these work is easily understood from a reference to Fig. 104, which shows a plan of one set of such flues. The main flue from the furnaces has a stopping door, D, fixed in it, and a number of parallel diagonal flues branch off from it on either side, the opening into

* *Eng. and Min. Journ.*, June 6, 1891.

† *E.g.*, at the Philadelphia S. and R. Works, Pueblo, Colo., where they have been only moderately successful.

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each from the main flue being very small, so as to divide the current of gases into approximately equal portions, which are again collected into the main flue by the gathering flues, G, on either side. In this way the velocity of the current in the parallel flues, which are narrower than the principal flue, is reduced to, say, one-tenth of that in the latter; while the surface exposed for condensation is twenty times as great.

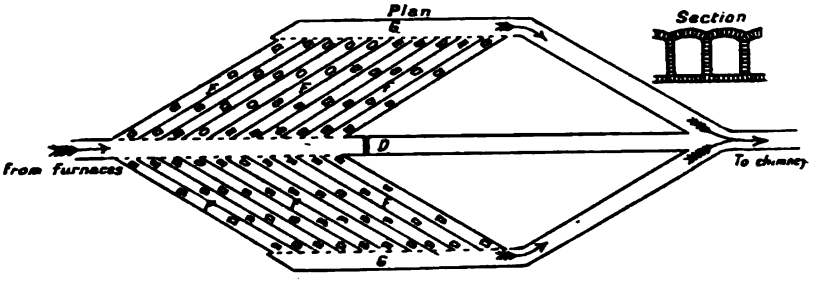

Fig. 104.—Cowper Flues.

An installation of this kind has been in use at *Linares* (Spain) since 1882, working most satisfactorily and yielding over 90 tons of fume in six months, containing 67 per cent. lead. The Cowper flues possess the very great advantage that the velocity of the current is reduced *simultaneously* with the increased surface offered to the gases, and therefore the fumes are under the most favourable conditions for deposition.

2. **Brushwood and Coke Towers.**—These methods were formerly largely employed, usually with the addition of a spray of water, but the product obtained is always in a very unsatisfactory form for handling, not to mention the great obstruction to the draught; they are now practically out of use.

3. **Freudenberg Plates.**—The Cowper flues may be multiplied and the individual flues narrowed to any desired extent, but a cheaper and simpler means of attaining the same end as regards increase of surface is by the adoption of Freudenberg plates shown in Figs. 105 and 106.* At the level of the springing of the arch flat iron bars, L, pierced with holes about 4 inches apart, are fixed across the flue by twisting the ends at right angles so as to enter the brickwork, and iron pins are driven into the holes so as to project about 1 inch on each side. Sheets of iron, B, No. 22 gauge, have pieces, D, rivetted to the ends of their upper side, in which loops are formed which drop on to the pins and so support the sheets in a vertical position 4 inches apart. Old sheet iron can be used for this purpose; in fact, old

* Egleston, *Trans. A.I.M.E.*, vol. xi., p. 379.

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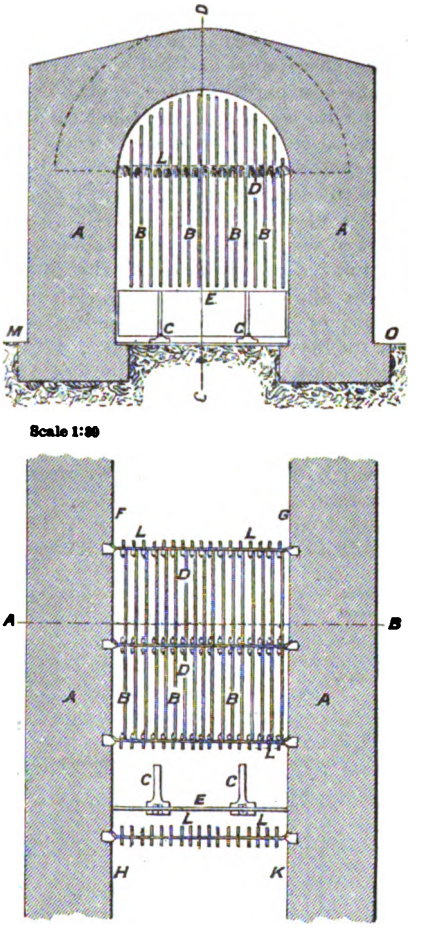
jig screens are commonly employed, while at the extreme end of the flue system, where the gases are cool, pasteboard has been found to answer when the flue dust is not ignited before removal. The flue-dust collecting on the plates falls to the ground on attaining a certain thickness, and at every 15 to 18 feet a cross partition, E, is erected in the lower part of the flue to prevent dust once collected from being taken up again by the air current and carried away into the stack. These cross partitions are of sheet iron bolted to cast-iron feet, C, and reach up in the flue about 20 inches.

The plates may be placed much closer together, but they are then liable to choke up, and the friction is so much increased that unless the chimney is of very great height and the flue runs uphill to it recourse must be had to increasing the chimney draught by artificial means. When 4 inches apart the ordinary draught is but slightly interfered with.

A good arrangement is to provide two or three parallel lengths of flue fitted with the Freudenberg plates, so that the current of gases can be either split up among the various flues or shut off at pleasure from one or the other for the purpose of cleaning, which has to be done so often that in the absence of some arrangement of the kind the furnaces may have to stop to allow of cleaning out the flues.



Figs. 105 and 106.—Freudenberg Plates.

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It might be supposed that thin iron sheets would rust very quickly, but this is not found to be the case where the gases are properly cooled, and where they pass through a long length of flue before reaching that part where the plates are placed, so that all the moisture is condensed out of them before they come in contact with the iron.

An installation of Freudenberg plates put in at the Muldner Hütte (Freiberg) in 1890 is described by Bauer * as a series of twenty-one parallel flues, each 33 feet long, forming part of the condensing system of the blast furnace and refining departments. The total surface of these flues is 1520 square metres; they are constructed of iron sheets fixed about 20 cm. apart. The sheets above the springing of the arch are fixtures, those in the central portion of the flue being suspended like those at Ems. The result of the insertion of the sheets was, that with an increase in ore smelted of 15 per cent., the flue-dust collected in the whole system showed an increase of 45 per cent.; the increase in that portion of the main condensing chamber containing the flues was no less than 82 per cent., while nearer the stack the quantity condensed was actually less than before. Unfortunately, there is no excess of chimney draught as at Ems; in fact, a Guibal fan has always been required to assist the natural draught, and it was found that an increase of 40 per cent. in the work of the fan was required to overcome the increased resistance caused by the plates. The Guibal fan used is 20 feet diameter and 3 feet 6 inches wide; it takes about 7 H.P. to drive it at the rate of 65 to 85 revolutions per minute, which gives a pressure equal to 34 mm. ($1\frac{3}{8}$ inches) of water, about 20 mm. of which corresponds to the resistance introduced by the plates. The cost of 20 mm. pressure is about £250 per annum, which, together with the interest and depreciation on the plant, must be set against the saving effected.

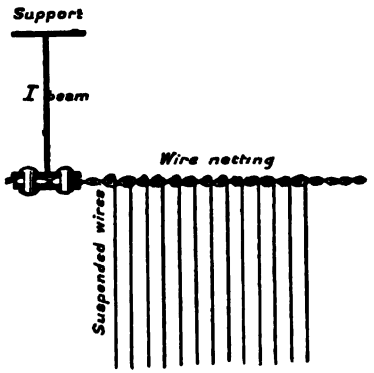

Fig. 107.—Rösing Wires.

4. Rösing Wires.—Instead of sheets of iron, wires may be used as first tried by Rösing.† The wires used are of No. 10 gauge, and three-fourths the full height of the flue; they hang in parallel rows from a wire netting of 1 inch mesh, which is rivetted to I beams running across

* *Jahrbuch für das Berg- und Hütten-wesen im K. Sachsen*, 1894, p. 39.
† Saeger, *B- u. H. Zeitung*, 1894, p. 299.

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the top of the flue as shown in Fig. 106. At the *Tarnowitz* Works an installation on this system in 1888 reduced the total amount of solid matter escaping during the year from 54 to 40 tons per furnace, without perceptibly influencing the draught, the extra material collected being very rich in lead.

5. **Use of Electricity.***—Since the discoveries of Lodge and Clark in 1884, it has been known in a general way that discharges of static electricity would rapidly cause all dust to settle in a closed chamber, and patents were taken out by the firm of Walker, Parker & Co. in 1885 for the purpose of utilising these discoveries practically. No success has hitherto attended experiments in this direction, because electrification of the dust particles can only take place in stagnant air; as soon as there is anything like a current of gases the discharge seems to be dissipated.

6. **Filtering Methods.**—So far as the author is aware we owe the first suggestion of filtering methods to Percy,† but it was not until recently that Bartlett experimented on the subject with satisfactory results. The Lewis and Bartlett bag process has been already described in Chapter v. As applied to blast furnace fumes the appliances employed have taken a somewhat different form, as, for example, at the *Globe Works* (Denver). The flue dust recovered at these works includes the whole of the lead fumes from the blast furnaces and roasters, and even that from the lead wells and slag taps, which is drawn off through an overhead main with funnel-shaped ventilators. It is ignited on the floor of the bag house, giving a porous grey cinder containing as oxides and sulphates Pb 75 per cent., Zn 3 per cent., Fe 0·5 per cent., As 1·3 per cent., and 4 ozs. silver per ton, which forms part of the ordinary smelting charge.

The *Brown-De-Camp* fume collector ‡ is on the same principle, and with it, as with all other filtering processes, it is necessary to thoroughly cool the gases down to 150° F. or less before their arrival at the condensing chamber; and advisable to settle out as much as possible of the ore dust and coarser clots of fume in ordinary flues and chambers. At the *Omaha* Works (Neb.), where the process has been in use since 1894, this is done by passing the gases from ten large blast furnaces, each 42 inches by 120 inches at the tuyeres, through 800 feet of brick flues. Instead of woollen bags a heavy open woven canvas or duck is employed, arranged in four high peaked ceilings, each 29 feet high by 99 feet long, and any one of which can be cut out of the series. A framework of I beams and pipes supports a series of ceilings in each compartment, the total effective filtering area of which is 40,000 square feet, and the capacity of each compart-

* Hutchings, *B. u. H. Zeitung*, 1885, p. 253; also Iles, *S. of M. Q.*, vol. xvii., pp. 109, *et seq.*

† *Metallurgy of Lead*, p. 449. ‡ *Eng. and M. J.*, Oct. 19, 1895.

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ment below the ceilings is 60,000 cubic feet. It is found that, to ensure complete efficiency, discharging the gases quite colourless and without visible vapour, about 16,000 square feet are required for each furnace, the whole installation being thus sufficient for ten furnaces. The fan is a 12 feet Murphy ventilator, which, at 200 revolutions, takes the fumes from ten furnaces, and consumes, roughly, about 7 H.P. for each furnace running. Suspended between the converging walls of the peaked ceilings are oscillating shafts carrying long beaters, which can be put in motion by means of levers from the outside of the building as often as the pressure gauge in each compartment shows that the meshes of the fabric are becoming clogged, causing the beaters to strike the canvas and shake off the dust, which falls to the floor of the building.

When the dust has accumulated to a sufficient extent it can be burnt on the floor, a separate set of flues and a small chimney being provided to carry off the products of combustion. It is usually, however, wheeled to a separate closed chamber for ignition, which converts it into a grey or pinkish friable coke, suitable either for the blast furnaces or for working up in the refinery together with skimmings and drosses to a *hard* lead.

The actual saving when running all the gases from seven furnaces through two compartments of the above condenser averages about 100 tons of metallic lead per month, carrying about 10 ozs. silver per ton, which is 6 per cent. of all the lead charged into the furnaces; this yields a gross income of about £1200 per month, or very much more than the total expense for maintenance, depreciation, and interest.

Wet Condensation.*—Many attempts have been made to employ water for condensing lead fumes, but the great difficulty is the practical impossibility of getting contact between the water and the minute particles of fume, which, instead of being attracted, are repelled by a moist surface as first noticed by Percy.† Three main varieties of wet process may be described:—

1. **Passing through Water.**—This is the most expensive, owing to the powerful fans required to force the fumes through the head of water. Simple bubbling through water under a diaphragm or through perforated pipes was soon found to be almost useless, but the method of the *Sheffield Smelting Co.* is very effective. The fumes are distributed in a closed tank by means of a network of perforated pipes 7 inches below the surface, and above the pipes are fixed several diaphragms of copper wire, gauge about 16-mesh, the action of which is to break up the bubbles and so increase the contacts of dust-laden gases with the water. The gases are forced along by means of Roots' blowers, and it is stated that the cost of the power required,

* *v.* Percy, *Metallurgy of Lead*, pp. 441-449.
† *Metallurgy of Lead*, p. 450.

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though considerable, is small compared with the value of the fume recovered.

2. **Blowing in Steam.**—This is cheap enough, but all the processes which depend upon the use of steam have proved utter failures. A large part of the steam escapes condensation, and rather hinders than assists the segregation of the dust particles, while such portion as is condensed forms a very acid mud which rapidly attacks the materials of the flues and chambers.

3. **Passing through a Water Spray.**—This process, though costly in plant, has given good results at several works. At the *St. Louis Smelting and Refining Works* the plant consisted of a chamber built of tiles, in sections containing shelves composed of drain tiles supported by planks borne on old iron rails. The smoke passed first up through one such tower and then down through another, being sprayed all the time through fine rose nozzles at the top of each tower. It was then driven through a long wooden tank containing water, and provided with a number of hanging curtains which forced the gases to come in contact with the surface of the water while they were again sprayed from above. The fans were two Sturtevants, 7 feet 6 inches diameter, and the fume was perfectly condensed, but whether the process ever paid or not is a moot point.

At the *Bimetallic Smelter* (Leadville) a similar plant is at work, consisting of two circular towers, each 20 feet high by 16 feet diameter, through which the fumes from two large pyritic furnaces are forced by means of two Huyett & Smith fans, 10 feet diameter, running at 260 revolutions per minute. The towers contain a great number of Λ-shaped tiles with serrated lower edges, supported in the form of shelves on old rails completely enclosed in sheet lead, the seams of which are "burnt" together, as are also those of the sheet-lead lining of the towers. Water is supplied from a shallow tank, forming the roof of the tower, through a network of 120 leaden pipes, and trickles down from shelf to shelf, falling from the serrated edges of one tile on to the ridges of those in the next row. The fumes enter the towers at a temperature of 350° to 400°, and leave at a temperature of 90°, being discharged through an octagonal stack 150 feet high built of planks heavily tarred. The condensed fume is washed out by the stream of water issuing from the bottom of the towers, settled in tanks, and sun-dried. It contains 25 to 40 per cent. Pb and about 25 ozs. Ag per ton.

Quantity of Flue-Dust Recoverable.—The quantity of flue-dust produced is influenced by various factors, among which may be mentioned the amount of fine ore in the charge, degree of friability of the fuel, pressure of blast employed, amount of bosh in the furnace shaft, care in keeping the walls free from accretions and the top cool, and, especially, the height of the column of charge in the furnace.

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With filtering methods, practically the whole of the lead volatilised can be collected as fume, but with all the other methods a variable amount always escapes, in many works little else but ore dust being collected.

At the *Keld Head* smelting works in 1857* the fume, collected by means of water-spray condensation from ores which yielded in the ore hearth 1374 tons of lead, gave 96 tons of fume lead, which is 7 per cent. of the ore yield, or about 5 per cent. of the total weight of ore charged, and over 6 per cent. of the weight of lead present.

Hofman† puts the average quantity of flue-dust *formed* in American works at 5 per cent. of the total weight of ore charged, which is probably an extreme figure for high modern furnaces; the quantity *collected*, however, averages barely half as much.

At Ems‡ in ten months of 1881-82, the 14,605 tons of ore treated, containing 42·8 per cent. lead, yielded 931 tons of flue dust, averaging 56·9 per cent. of lead; the flue-dust actually collected, therefore, was 6·4 per cent. by weight of the ore treated, and contained 8·5 per cent. of the lead contained in it. At Freiberg‖ in 1893 the weight of fume actually collected amounted to no less than 9·7 per cent. of the weight of ore smelted, and contained 1658 tons lead, 36,655 ozs. silver, and 917 tons of white arsenic, the total value being £13,636.

It has been already mentioned that at Omaha (with the new appliances) the fume collected, as an extra saving over and above the ordinary flue- and chamber-dust collected in 800 feet of flue, is equivalent to 6 per cent. of the lead charged into the furnace. It may, perhaps, be reckoned that, as a rule, in works smelting ores fairly rich in silver, from 2 to 3 per cent. of both lead and silver will be carried away mechanically as fine dust, which can all be settled out readily in suitable chambers; while from 6 to 10 per cent. of the lead, and ¼ to ½ per cent. of the silver, will be volatilised, more or less of which is condensible according to the degree of perfection of the appliances employed. With ores poorer in silver, the quantity of that metal volatilised is much greater in proportion to the lead, and may reach, or even exceed, one per cent. of the total amount present.

TREATMENT OF FLUE-DUST.

The methods adopted for treating flue-dust have nothing to do with the mode of collection. The use of lead fume in its natural condition as paint is more than two centuries old, and at Linares and other places large quantities are sold for use as such, but the grey colour is frequently objectionable. The

* Percy, *op. cit.*, p. 456. † *Op. cit.*, p. 282.
‡ Egleston, *Trans. A.I.M.E.*, vol. xi., p. 404.
‖ Bauer, *Jahrbuch f. d. B. u. H. W. im. K. Sachsen*, 1894, p. 39.

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special treatment of non-argentiferous flue-dust obtained from the Scotch hearth to produce a white paint has been already described in Chapter v., but with ordinary flue-dust the object must be to return it to the ore furnace, so as to obtain the lead and silver it contains in the form of metal.

The commonest way of handling flue-dust is, perhaps, a simple wetting down, forming a sort of mortar, the lumps of which, after partial air drying, resist disintegration to such an extent as to enable the heat to act upon them. Ignited flue-dust in particular forms coherent lumps which are in very good condition for the furnace. At the various *Broken Hill* plants where lead is cheap and fuel and labour dear, this has been hitherto the only means adopted for handling the flue-dust, though it is well known that much of the finer portion is simply blown out again by the blast. Where lead is, comparatively speaking, more valuable, it is preferable either to make the flue-dust into bricks before smelting, or to fuse it down in the fuse box of a slag-roaster, or in a separate reverberatory furnace.

1. **Bricking.**—One of the commonest methods of bricking is with lime, of which 5 to 10 per cent. is mixed with the flue-dust in a pug mill, the bricks formed in a simple machine and dried in the sun. The bricks are very "tender," unless they are made in a machine which exerts considerable pressure upon them. Much stronger bricks are made by substituting clay for lime, as was done formerly at *Eureka* (Nev.). This process is in use at the *El Paso* Works, where 5 per cent. of clay is found to be sufficient; the bricks, though made by hand and simply air dried, stand a fair amount of handling, and the cost is only 12s. per 1000 bricks of ordinary size.

Pan-slimes (85 per cent. quartz, 2 or 3 per cent. clay) were used as binding material at Tombstone (Ariz.) by Church,* who found that the bricks were sufficiently coherent, though made only by hand and sun-dried, and attributes the binding quality of the slimes to their extreme fineness. The fine roasted ore from the leaching tanks at Goslar (Lower Harz), after washing to remove the zinc sulphate, becomes quite hard and coherent when left to dry in piles. Similar results have been noted with roasted pyrites at Rio Tinto and other places.

A solution of green vitriol (ferrous sulphate) has long been employed in Continental works for agglomerating fine ore, and Hahn found that it did very well for flue-dust. The sulphur so added to the charge is, however, objectionable from its reduction to matte, and Hofman † suggests that the simultaneous addition of slaked lime would be an improvement, as the ferrous hydrate precipitated would become gradually oxidised on exposure to the air, and so form hard lumps. Dilute sulphuric acid is found by

* *Trans. A.I.M.E.*, vol. xv., p. 611. † *Op. cit.*, p. 292.

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Eurich * to form a very good binding material on account of the basic sulphates formed.

Simple pressure (as in dry-bricking machines) has been applied by Peters† to the bricking of fine pyritic ores with good results. The same method is employed at the *Pennsylvania* Works (Utah), the flue-dust being mixed with fines of rich ore.

At the *Germania* Works (Salt Lake, Utah) the flue-dust is mixed in a slightly damp condition with enough lime to make 5 per cent. CaO in the final brick, and is then fed into the hopper of a double-plunger pressure brick machine, which forms flat circular cakes about 4 inches diameter, and weighing 3 lbs. each. Of these, 4,200 per hour are turned out, the total capacity being thus about 55 tons in a ten hour shift. The cakes are air dried, generally for a couple of days only, owing to want of space, but are better if left to dry for a week.

At *Mansfeld* a flue-dust containing as much as 14 per cent. lead is produced from the copper schist in smelting for copper matte. It is machine-bricked with raw bituminous fines produced in mining the copper schist, and smelted with ferruginous matte slags in a small blast furnace to work-lead, containing over 100 ozs. silver to the ton.

At *Goslar* the flue-dust contains so much zinc oxide that this is first leached out with dilute sulphuric acid, and recovered as white vitriol from the liquors, while the lead and silver are concentrated in the residue, which is bricked for the ore furnace.

2. **Fusion.**—A common way of handling flue-dust is to add a few cwts. of it to every charge of roasted ore on the slagging or sintering hearth immediately before dropping the charge. In this way very little is carried away by the draught, but there is a considerable loss of lead by volatilisation.

At *Mazzaron* (Spain) the flue-dust is bricked with fine galena, lime, and a little sand, before being added to the charge on the last hearth of the reverberatory roasting furnace; the object being to still further diminish the mechanical loss in charging and mixing.

At the *Globe* Works a small *separate* reverberatory is used for melting down flue-dust, the fumes being all collected and filtered in the bag house. A very good slagged product is made, but the loss of lead (25 per cent.) would be prohibitive, were it not for the advantage of being able to save it all by filtering.

On the whole, this method must be regarded as decidedly preferable to bricking, for, in the latter method, not only is there the mechanical loss from the bricks crushing under pressure, but also a considerable volatilisation loss caused by reduction of metallic lead high up in the furnace through intimate contact of its oxide with carbonaceous particles in the flue-dust. In the

* *Private Communication*, May, 1896.
† *Modern Copper Smelting*, 7th ed., 1895, p. 357.

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fusion hearth this carbonaceous matter is partly burnt direct and partly consumed by Fe_2O_3 in roasted ore.

Flue dust is in most cases combustible, smouldering readily on ignition, a property due in some cases to the presence of finely disseminated carbonaceous particles, but more often to finely divided sulphides, especially PbS. The flue-dust caught in the lead works at *Cartagena* (Spain)* is ignited in the flue before withdrawal, forming adherent crusts. Analyses of both the crude and the calcined product are given in Table XXXI. Ignition is adopted at many other places, and, in particular, the fume recovered by bag filtering processes is always ignited on the floor of the bag house before removal, or in a separate chamber, thus forming a crisp cinder suitable for the furnaces.

CHAPTER XIII.

COSTS AND LOSSES—PURCHASE OF ORES.

Costs of Working.—The cost of smelting lead ores varies very greatly, the principal factors which affect it being:—

1. The chemical composition of the ore, its physical condition (coarse or fine), and its richness or poverty in lead.
2. The cost of labour at the smelting centre.
3. The cost of fuel and fluxes delivered at the works.
4. The cost of refining locally, or of getting the product to a refining works at a distance.

Taking the case of a so-called "neutral" or self-fluxing ore, in which the percentages of silica and of iron are equal, with sufficient lead (10 per cent.), and not over 4 or 5 per cent. of sulphur, so that it can be smelted without roasting, the custom at the large works in Denver and Pueblo is to reckon $4.50 per ton of 2000 lbs. as the bare cost of treatment.

Labour.—Each furnace of from 33 by 84 inches up to 42 by 140 inches requires per twenty-four hours the following staff:—Three feeders and furnace-keepers (8-hour shifts), four charge wheelers and four to six slag pullers (12-hour shifts), as well as four to eight labourers on the dump, sorting slag, &c.

The regular wages in Denver are—Furnacemen, enginemen, and foremen, $3 to $4 (12s. 6d. to 16s. 8d.) per day of twelve hours; feeders, wheelers, &c., $2.50 (10s. 5d.) per day of twelve hours; labourers, $1.75 (7s. 3d.) per day of ten hours. Coke cost $6 to $7 (29s.) per ton; limestone, with 50 per cent. excess CaO, $1.25 (5s. 3d) per ton; iron ore, with 70 per cent. excess

* Sanchez y Massia, *Metalurgia del Plomo*, Madrid, 1894, p. 293.

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FeO, $5 (20s. 10d.) per ton; and coal (slack) for boiler fuel, $1.50 (6s. 3d.) per ton. At these prices the cost of smelting on a large scale (say, 400 tons per day and upwards) will be nearly as above stated, the items being as follows:—*

Labour,	$1.90 =	7s. 11d.
General expenses, assaying, and management,	0.27 =	1s. 1½d.
Fuel for power,	0.10 =	0s. 5d.
Coke (15 per cent. on ore charge),	1.36 =	5s. 8d.
Limestone, say three-tenths ton,	0.37 =	1s. 6½d.
Interest, depreciation, and repairs,	0.50 =	2s. 1d.
Total,	$4.50 =	18s. 9d.

At Leadville and in Salt Lake City the prices of fuel and labour are higher, so that $6, or, say, 25s., is often reckoned as the cost of smelting an ore which has not to be roasted.

At *Broken Hill, N.S.W.*, coke costs 57s. 6d. to £3 per ton; limestone flux (92 per cent. $CaCO_3$), 14s.; iron flux, with 10 per cent. SiO_2, 22s. 6d.; and common labour, 8s. per day for 8-hour shifts. No details as to smelting costs are published by the Proprietary Company, but from data given in the annual reports it may be calculated that the cost is somewhat as follows:—Labour and superintendence, 6s. 3d. per ton; flux, 4s. 6d.; coke (12½ per cent. of charge = 22·7 per cent. of ore), 13s. 3d.; making a total of 24s. per ton; to which has to be added, say, 6d. per ton for power (blowing and pumping), and, perhaps, 1s for depreciation of plant, repairs, and replacement; so that the total cost cannot be less than about 26s. per ton. At Port Pirie the cost is, of course, lower, owing to the lower prices of coke and fluxes, but then the cost of railway transit on the ore must be added, so that the total expenses cannot be much less.

C. Henrich † gives $7.03 (29s. 3½d.) as the cost of smelting in a single furnace, 33 by 84 inches, at the rate of 48 tons per day, an ore requiring one-third of its weight of limestone flux, costing 12s. 6d. per ton, with 18 per cent. of coke, costing £1 per ton.

At some places, owing to cheaper labour and fuel, the total cost is much lower than this; while at others, where fuel is dearer, the cost is higher. It should be borne in mind when statements are made as to exceptionally low costs that frequently the "cost of smelting" is put down at the bare figures for labour, fuel, and fluxes alone, without any allowance for power required, for general expenses of management, or for repairs, interest, and depreciation.

The above figures refer to the smelting of ores which require no roasting. The cost of roasting at Denver or Pueblo varies

* Furman, *S. of M. Q.*, vol. xv., p. 3.

† Quoted by Fraser & Chalmers in their catalogue.

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from $1 (4s. 2d.) in automatic furnaces up to from $1.50 to $2 (8s. 4d.) in the ordinary hand furnaces, but to these figures something must be added for re-treating flue dust, and on account of the sulphur left in the ore, which forms matte, and so adds to the expense of treatment. When ores have to be fused, the average cost may be reckoned at not under 10s. 6d. per ton under Colorado conditions. The total cost of treatment in the case of a neutral sulphide ore which requires roasting will thus be brought up to a total of $7 (29s. 2d.) at Colorado prices.

Smelting Charges.—The cost of smelting an ore is largely influenced by its chemical composition; in calculating the actual cost on any particular ore a certain amount per ton is credited or debited for each per cent. (unit) of various constituents. Thus in Colorado and other Western American centres, the following are the average values adopted :—*

	Debit. Cents.	Credit. Cents.
Silica, per unit,	10 to 15	...
Iron and manganese, per unit,	...	10 to 15
Lime, per unit,	...	6 to 10
Magnesia and baryta, when under 10 per cent.,	...	as lime.
Zinc, per unit,	30 to 50†	...
Barium sulphate, over 10 per cent., per unit,	5	...
Arsenic, per unit,	50	...
Sulphur (if no charge is made for roasting),	15	...

Taking, for example, the case of an ore containing :—

SiO_2.	Fe.	CaO.	Zn.	$BaSO_4$.	Mn.	S.	Ag.	Au.	Pb.
14	6	8	7	24	4	10	60 oz.	0·2 oz.	21 per cent.

the bare cost of treatment would be calculated by the smelter as a basis for purchase somewhat as follows :—

	Debit.	Credit.
Silica excess over iron, 14 – 6 per cent. = 8 per cent. at 15 cents,	$1.20	...
Manganese, 4 ,, ,, 15 ,,	...	$0.60
Lime, 8 ,, ,, 10 ,,	...	0.80
Zinc, 7 ,, ,, 30 ,,	2.10	...
$BaSO_4$, 24 ,, ,, 5 ,,	1.20	...
Sulphur, 10 ,, ,, 15 ,,	1.50	...
Ordinary smelting cost per ton,	4.50	...
Balance, being nett cost of treatment,	...	9.10
	$10.50	$10.50

The above $9.10 is the actual cost at the works, to which must be added a certain amount for profit; usually $7 instead

* *v.* Furman, *loc. cit.*; Hofman, *op. cit.*, p. 74; Brunton, "Correspondence on Smelting Processes," *Proc. Inst. Civ. Eng.*, vol. cxiv., part ii.

† Frequently under 8 per cent. of zinc goes free; over 8 per cent. the entire contents are charged for at 50 cents per unit.

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of $4.50 per ton is the basis rate calculated to cover profit and smelting losses as well as bare cost.

Some ores in special demand are, however, purchased by the smelting works on terms much more favourable to the producer. Thus, the gold bearing pyrites concentrates of Gilpin County, Colorado, containing under 10 per cent. SiO_2, were for a long time eagerly purchased by Denver smelters at a smelting rate of $2.25 per ton, which barely covers the cost of roasting;* and 95 per cent. of both gold and silver contents are paid for at New York prices.

Losses.—The losses in smelting are—(1) In slag thrown away; (2) in flue dust and fume incompletely recovered; (3) in bye-products, matte, speiss, flue-dust, &c., which suffer further treatment losses before they can be brought into a marketable condition.

When producing a lead bullion of about 300 ozs. Ag per ton, perfectly clean slags will run as low as $\frac{3}{4}$ per cent. lead by dry assay and $\frac{1}{2}$ oz. silver to the ton; the general average, however, in fairly good work is probably not much under 1 per cent. lead and $\frac{3}{4}$ oz. silver, while carelessness in working up the charges or neglect on the part of the furnace foreman may easily result in the production of slags which separate imperfectly from matte and contain 2 per cent. lead and $1\frac{1}{2}$ ozs. of silver; especially if the ore be somewhat rich in lead, and the furnace one of the old type with comparatively low column of charge and pressure of blast.

In some cases, where fuel and flux are dear (as, for example, at Broken Hill, N.S.W.); or where the ore charge is very rich in zinc, it may even be better policy to throw away slags containing 3 or 4 per cent. lead than to attempt to clean them by a further expensive consumption of fuel, and the addition of barren fluxes, with the attendant reduction of furnace capacity to which they give rise. The average percentage loss of silver and lead in slags on a charge containing 10 per cent. lead and 30 ozs. silver may be reckoned at not much less than 10 per cent. of the lead and 1 per cent. of the silver as calculated by the results of the commercial uncorrected dry assays, which are, as has been shown, far below the truth.

With regard to slag losses, it is desirable to bear in mind that losses which would be intolerable at Swansea, at Freiberg, or at Denver, may actually indicate the best possible practice in remote parts of the west, in the wilds of Mexico, or in South America. The object of the metallurgist should be to make the largest possible profit per ton of ore treated, and if it is more profitable to produce a slag with 6 per cent. lead and 4 ozs. silver per ton than to flux the charge in such a way as to make a cleaner slag, as is the case to-day in parts of Central and

* The rate has been recently raised by $1 to $2 per ton.

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Southern America, then the foul slag is the proper slag to make. As Lang puts it,* "It is always pecuniary profit, and not the perfection of processes, which is the criterion of metallurgical fitness."

With regard to the loss in uncondensed fume there is room for more doubt, and the *real* loss is always much greater than the *apparent* loss shown by the ordinary dry assays for lead and silver. In connection with this matter, reference should be made to Chapter ii., in which is recorded the fact that the ordinary dry assay for silver gives results which, in the case of a mixture of ordinary ores containing from 5 to 100 ozs. and averaging about 50 ozs., are below the truth to the extent of 7 or 8 per cent. of the total present; while the dry assay for lead with an ore mixture of 12 per cent. is on the average low to a greater extent, probably 10 or 12 per cent. of the total present. The *real* loss in uncondensed flue-dust is, therefore, as has been pointed out among others by Egleston,† much greater than it is usually supposed to be.

According to Hofman,‡ the total apparent loss of lead in good work is 7 per cent., though it not uncommonly reaches twice this amount (corresponding with real total losses of 15 and 23 per cent. respectively). As regards the total apparent loss of silver, Hofman says it "rarely reaches 5 per cent.," which would indeed be quite an outside figure. That the real loss of silver is, however, much greater than that shown by assay, is proved by the fact that at some establishments the silver produced is more than that shown by the assays which have served as a basis for purchase. This, however, does not so much indicate perfection in the smelting as imperfection or bias in the assaying. As regards the loss of lead in uncondensed fume, which is so much greater than the corresponding loss of silver, a large proportion could be saved by filtering appliances, but in many places it would hardly pay to use them.

The following table shows the *apparent* percentages of silver and lead obtained from the ore at various metallurgical works, as admitted by the furnace managers.

Keen competition among smelters in America has led to greater care in assaying, American assayers commonly cupelling at a lower temperature than their *confrères* in Europe, with the object of partially compensating for the cupel loss, and so getting a nearer approximation to the truth. It is to this cause that the apparently higher loss of silver in American works should undoubtedly be attributed.

* *Matte Smelting*, New York, 1896, p. 72.
† *Trans. A.I.M.E.*, vol. xi., p. 379.
‡ *Op. cit.*, p. 293.

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TABLE XXXII.—Apparent Percentage Yield of Silver and Lead.

	Pontgibaud, 1874. (1).		Clausthal, 1887. (2).		El Paso, 1892. (3).		Average good American Work, 1897. (4).	
	Lead.	Silver.	Lead.	Silver.	Lead.	Silver.	Lead.	Silver.
Grade of ore treated,	40 °/₀.	96 ozs.	50 °/₀.	23 ozs.	13 °/₀.	40 ozs.	11 °/₀.	...
Percentage yield :—								
In work lead,	80·04	102·28	} 80·92	87·01	} 81·2	86·9	...	...
In foul slags,	2·04	0·66					...	...
In flue-dust,	3·67	0·56			5·0	2·6	...	...
In matte,	...	...	10·14	13·22	3·8	7·5	...	...
Total yield,	85·75	103·5	91·06	100·23	90·0	97·0	90·0	98·5
Loss or gain on commercial assays,	− 14·25	+ 3·5	− 8·94	+ 0·23	− 10·0	− 3·0	− 10·0	− 1·5

References.—1. Phillips, *Elements of Metallurgy*, 1874, p. 563. 2. Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 407. 3 and 4. *Private notes.*

Purchase of Ores—Western Smelters' Sliding Scale.—The system of ore-purchase varies greatly in accordance with local conditions and local customs; but the schedules in use throughout the Western States of America are typical and may be described in detail as capable of almost universal application with slight modifications. All the assays are uncorrected dry assays, and the basis of the calculation is the assumed mean price of lead in New York ($4 per 100 lbs. = about £9, 10s. per ton in England). At this price for lead, ores are bought according to the following scale :—

Under 5 per cent. lead				at nothing.	
5 per cent.	and under	10 per cent.		25 cents per unit of 20 lbs.	
10 ,,	,,	20 ,,	,,	35 ,,	,, ,,
20 ,,	,,	30 ,,	,,	40 ,,	,, ,,
30 ,,	,,	40 ,,	,,	45 ,,	,, ,,
40 ,,	,,	50 ,,	,,	50 ,,	,, ,,
50 ,,	and over			55 ,,	,, ,,

The *gross* value of a 50 cent lead ore at the price of $4 per 100 lbs. is 80 cents per unit, but the smelter retains 25 cents per unit (or £5, 4s. 2d. per ton) to cover smelting losses, refining charges, and freight to Eastern markets. It is obvious that these losses and charges will be greater in proportion on the poorer ores; hence the above scale. It is further provided that for every 5 cent per 100 lbs. fluctuation in the New York price of lead an allowance shall be made of 1 cent per unit in the

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above scale up or down. When lead ores are scarce the above scale is modified, sometimes to the extent of paying 50 cents per unit on everything over 20 per cent. in the case of good carbonate ores which are very much in demand.

As to silver, 95 per cent. of the assay contents of all ores is paid for at New York quotations on the day of settlement, which means that lead ores have to pay the bulk of the refining charges on the silver of the dry ores. Gold is paid for without deductions at $19, or now usually $20 per oz. fine, which is 96·6 per cent. of the full Mint value ($20.67 per oz.).

As a rule, copper is not paid for in lead ores, but of late years competition has forced some of the smelters to pay for this metal when over 5 per cent., at about $1.20 or $1.30 per unit, which is something like one-half of its gross value.

As an example, the value of the ore already quoted a few pages back may be calculated according to the above schedule:—

Lead, 21 units at 40 cents per unit, ...	$8.40
Silver, 95 per cent. of 60 ozs. = 57 ozs. at, say, 66½ cents,	37.90
Gold, $\frac{3}{5}$ oz. at $20, ...	4.00
	$50.30

The true cost of smelting the above ore having been already ascertained to be $9.10 per ton, the smelter would probably quote a "treatment charge" of $12 per ton, and the price at which the ore was purchased would be:—

Gross value per ton as above, ...	$50.30
Treatment charge, ...	12.00
Net value per ton, ...	$38.30

The smelters' profit may vary from $1 to $3 per ton, according to the nature of the ore and the amount of competition for that class of ore at the moment; thus carbonate lead ores with ferruginous gangue are frequently treated without charge, or even sometimes at a positive loss, which is made up by increasing the treatment charge on the dry ores.

As a rule, throughout the Western States outside of Colorado, no attempt is made to calculate the actual cost of treatment of true lead ores at the particular locality; but, in order to prevent ores from being shipped to Colorado, it is customary to take as the normal smelting charge the Denver or Pueblo rate *plus* the cost of transit to either of these points, when a small deduction will turn the scale and prevent ores being shipped away from local works.

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CHAPTER XIV.

THE TREATMENT OF ZINC-LEAD SULPHIDES.

REFERENCE has been made in Chapter viii. to the difficulty of treating, by the ordinary roast and reduction process, such argentiferous lead ores as contain 20 per cent. and upwards of zinc, except by diluting or smothering them with an admixture of purer ores. The object of almost all attempts at treating such material has been to remove the zinc in solution so as to smelt the plumbiferous residue more easily and with less loss.

Concentration.—It is probable that very few, if any, of the zinc-lead sulphide ores contain galena and blende so intimately mixed as put them entirely beyond the reach of the ordinary dressing processes to separate a notable proportion of the galena in a condition suitable for smelting. Concentration, therefore, should always be the first step in the treatment of such ores; unfortunately, however, not only is a large amount of "middlings" produced, which it is quite beyond the power of ordinary dressing machinery to separate, but there is a great loss of both lead and silver in fine slimes, the whole of which have, therefore, to be carefully settled and collected for smelting.

Concentration at Broken Hill.—As regards Broken Hill sulphides, the dressing plant is generally arranged much on the lines familiar in European and American practice, except that the crushing is not so fine; that the slime treatment is quite insignificant owing to the fact that the slimes are, in any case, so rich in silver as to be worth collection and smelting; and that a small number of very large jigs, treating practically unsized pulp, are found to do quite as perfect and more economical work than the large number of small jigs working on carefully classified sizes which have been the characteristic of German and American practice.

Thus the concentrating plant of the *Broken Hill Block 14 Co.*, the capacity of which is 2500 tons per week, consists of two Blake jaw-crushers, each followed by a pair of rolls, 33 inches diameter and 20 inches face, crushing through 10-mesh with the help of a stream of water, any coarse particles being separated by a trommel and returned to the rolls by an elevator. From the rolls the pulp passes without classification to four large jigs of the "Hancock percussion" pattern, the hutches of which are

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25 feet long by 4 feet 6 inches wide, and the moving shaking sieves 20 feet long by 3 feet 3 inches wide. The galena from the first hutches of these jigs is very clean, and the tailings are sufficiently low in lead and silver to be at present rejected as not worth further handling, though, no doubt, they will be valuable at some future date.

The middlings from the first series of jigs pass over a second series of smaller jigs of the same pattern, which yield a second concentrate not quite so rich in lead as that from the first jigs and a somewhat richer tailings. The slimes are passed over convex round tables which save some of the coarser particles of suspended galena; the finer slimes are collected in suitable settling tanks and slime-dams and smelted together with the concentrates.

The original ore treated by the Block 14 Mill varies a good deal in composition, but averages 22 per cent. Pb, 16 per cent. Zn, and 13 ozs. Ag per ton. The products are:—*

	Lead.	Zinc.	Silver.
	Per cent.	Per cent.	Ozs. per ton.
First grade concentrates, .	60 to 70	8 to 10	25 to 30
Second ,, ,, .	45 ,, 55	15 ,, 20	20 ,, 25
Middlings, ...	12 ,, 14	30 ,, 37	10 ,, 15
Tailings, ...	3 ,, 7	8 ,, 12	3 ,, 8
Fine slimes, ...	30 ,, 35	15 ,, 25	20 ,, 25

As a rule, it takes from 3½ to 4½ tons of ore to produce 1 ton of concentrates, and the ore yields 10 per cent. of fine slimes. The total cost of concentrating and handling is 2s. 7d. per ton.

Of the above products No. 1 is at present shipped to England, Nos. 2 and 5 are shipped to the company's smelting works at *Port Adelaide* to be roasted and smelted in blast furnaces;† No. 4 is for the present rejected entirely, great part being hoisted up an incline and shot down an old shaft for filling underground. As to the middlings they are at present being stacked pending a decision as to the most satisfactory way of treating them. Some cargoes have been already re-jigged up to 37 per cent. Zn and sold in Europe to the spelter works as low grade blendic ore, but it is probable that arrangements will be eventually made for dealing with them in Australia.

Smelting of Concentrates.—The smelting of fine concentrates after roasting in blast furnaces is accompanied by various inconveniences and by considerable losses in foul slags and flue dust, which can only be reduced by employing a very large amount of

* Information supplied through the kindness of the manager, T. J. Greenway.

† *v.* Chapter xi., where the practice is described at length.

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lump ore. The author has suggested * that a more economical method of handling these concentrates with less loss of lead, and especially of silver, would be a modification of the roast-reaction process carried out at some point where cheap coal was attainable. The proposed method consists in roasting as thoroughly as convenient a certain proportion, say three-fifths, of the material to be treated and charging it while still red hot from the roaster, together with the remaining two-fifths of unroasted concentrates, into a reverberatory furnace of large size built like a softening furnace inside a wrought-iron tank, to hold the bath of lead, which would remain permanently in the bottom of the furnace, like the bath of matte in modern copper smelting reverberatories. Reaction would take place on rabbling the charge, and, after a short settling, the slag would be skimmed and set aside for smelting in the blast furnace together with ferruginous, coppery, antimonial, arsenical, and other mixed ores of the precious metals, the usual fluxes being employed according to the composition of the ore mixture. This modification of existing methods demands cheap coal and, in order to get the full advantage of it where lead is dear, some fume-filtering appliance for the furnace fumes.

Treatment of Zinc Middlings.—It is probable that first-grade lead concentrates will always be treated by smelting, and the so-called "sulphide problem" (that is, the problem of treating zinc-lead sulphides poor in silver) resolves itself into the question of treating "middlings" with 12 to 20 per cent. Pb, 30 to 35 per cent. Zn, and 10 to 15 ozs. Ag; and "slimes" with 30 to 35 per cent. Pb, 15 to 25 per cent. Zn, and 20 to 25 ozs. Ag.

The processes proposed (most of which have been designed for the treatment of original ores direct without any concentration) are very numerous,† but it will only be necessary to describe here those which appear to have offered some approach to commercial practicability. They may be conveniently considered under the following heads, viz.:—A, Dry Methods; B, Chemical Methods; C, Electrolytic Methods.

A. DRY METHODS.

1. **Distillation Processes.**—The ore mixed with a reducing agent is charged into vertical or inclined retorts and distilled upwards, leaving lead and other metals in the residue. This method is adopted on a large scale at Freiberg, but is too expensive as regards labour, fuel, and retorts to be available at

* *Trans. Australian Inst. of Mining Engineers*, vol. iv., 1897.

† *v.* Hofman, *op. cit.*, p. 147, *et seq.*; Schnabel, *op. cit.*, p. 329; Emmens, *Min. Ind.*, vol. i., pp. 316, *et seq.*; vol. iii., p. 432.

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most other smelting centres, as, for example, those of the United States, Australia, or Mexico.

The process proposed by **Hunicke***—viz., pre-heating the ore and coke, and then charging them into a blast furnace—has not hitherto come into practical use, though it appears to contain a germ of possible future utility.

2. **Bartlett's Process.**†—Various air-blast processes have been proposed, but that here described in use at Cañon City, Colo., is the only one which has been really successful. The ores treated are the mixed blende-galena ores rejected by Denver smelters, and, though varying widely in composition, average Zn 30 per cent., Pb 8 per cent., Cu 1 to 2 per cent., Fe 10 to 20 per cent., SiO_2 12 to 20 per cent., Ag 10 to 20 ozs. per ton, Au, say, $\frac{8}{10}$ oz. per ton. The process consists of two stages, besides the subsequent treatment of the fume.

In the *first stage*, the ore, crushed to pea size or smaller, is mixed with 75 per cent. of its weight of fine coal in a tube with a worm screw. It is then moistened, and in charges of 600 lbs. is "blown up" in a perforated cast-iron grate, the thickness of the layer being about 4 inches, and the pressure of air employed about 2 ozs. The charge is not stirred in any way, and during oxidation it, to some extent, sinters together. Complete elimination of sulphur is not aimed at, and the blast is always stopped when 10 per cent. of this element still remains in the residue, as otherwise the loss of silver by volatilisation would be too great. When As, Sb, Se, or Te are present, the loss of silver is considerable, but in the absence of all these elements comparatively little silver is carried away by the blast.

The fume is condensed in bags arranged similarly to those described and figured in Chapter v. in connection with the "Lewis and Bartlett process." It contains sulphides, sulphites, and sulphates of both lead and zinc, as well as traces of other elements; it is roasted with free access of air in a long tube in which a worm screw is kept moving, by which means traces of carbon as well as of arsenic, antimony, mercury, selenium, cadmium, and other elements are driven off, and the resulting dense white compound, containing 55 to 60 per cent. zinc oxide and 35 to 40 per cent. of basic lead sulphate with 4 to 5 ozs. silver per ton, is ground and sold as white lead substitute.

In the *second stage* the cinder or semi-scoriaceous residue resulting from the blowing up, and containing still ZnS 12 to 15 per cent., Pb 1 per cent., Cu 1 to 2 per cent., Ag 10 to 20 ozs., the balance being chiefly iron oxide and silicate with some FeS and free SiO_2, is smelted in the Bartlett blast furnace, together with any plumbiferous or zinciferous copper ores

* *E. and M. J.*, Dec. 24, 1892; Sept. 15, 1894.

† *Colo. S. S. M. Sci. Q.*, vol. ii., p. 1; also *E. and M. J.*, Oct. 7 and Dec. 9, 1893.

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which may be obtainable at a cheap rate, and 5 per cent. of lime, iron ore being also added when the mixture is too siliceous. The Bartlett furnace is peculiar in having two rows of small tuyeres, one about 10 inches above the other; the lower tuyeres, directed downwards, serve to scorify the molten bath immediately below their level, while the upper row is directed upwards, with the object of driving the heat up and preventing the condensation of zinc in the upper part of the furnace. The furnace is run hot with a low column, a powerful blast, and a comparatively siliceous slag (35 to 42 per cent.), so as not to carry away the zinc into the slag; but rather to volatilise as much as possible of the remaining zinc contents of the mixture amounting to from 12 to 20 per cent., as well as whatever lead may be present. The resulting slag contains 2 to 7 per cent. zinc and $\frac{3}{4}$ oz. silver per ton; but is practically free from lead and gold. The matte produced contains 30 to 40 per cent. Cu, 2 to 4 per cent. Zn, 75 to 200 ozs. per ton silver, and $\frac{1}{5}$ to $1\frac{1}{2}$ oz. gold. The fumes from the blast furnace, after settling out the coarse dust, are forced through a bag house similar to that used for the fumes from the blowing-up hearth.

The cost of treatment at Cañon City is given at $6 (25s.) per short ton, with coke at 21s. and slack coal at 2s. per ton. The loss of silver does not average more than 2 ozs. per ton, or, say, 15 per cent. of the total present in these low-grade ores; gold and copper usually show a slight plus—not, however, because there is no loss, but on account of traces of both metals in some of the ores not being reckoned or paid for; the maximum loss of copper is thus reduced to less than $\frac{1}{2}$ per cent., and even that of zinc is under 7 per cent. The greatest drawback to the process is the limited sale of the high-class pigment produced; according to Bartlett,* 50 tons per day (produced from 200 tons of ore) is the maximum which the American trade will absorb.

3. **The Burnham Syndicate Process.**—This process, founded on the patents of Fry, Angell, and Ellershausen, consists in its latest form of smelting the mixed sulphide ore in ordinary lead furnaces, together with certain proportions (perhaps one-fourth) of oxide of iron and salt cake. The salt cake is presumed to be transformed in the furnace into caustic soda, which then, together with more iron oxide, acts upon the sulphide of zinc, and carries away the zinc into the slag, the iron combining chiefly with sulphur to form matte, while the lead is reduced to metal. It is obvious that the addition of so powerful a base as soda will assist the zinc in becoming slagged together with the other bases, but highly probable that the advantage obtained will be insufficient to compensate for the increased cost. One more

* *Colo. S. S. M. Sci. Q.*, vol. ii., No. 1.

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drawback to the process is the comparatively large quantity of low-grade iron matte produced, which would undoubtedly carry away some silver and copper without being rich enough to pay for re-treatment.

B. CHEMICAL METHODS.

1. **The Grimm Process.***—This oldest and simplest of all wet processes, first tried by Grimm at Przibram, is still in use at Goslar (Harz) for treating the Rammelsberg ores. The ore mixture contains 27½ to 30 per cent. blende, 9 to 12 per cent. galena, 1 to 1¾ per cent. chalcopyrite, 8 to 12 per cent. pyrites, 45 to 49 per cent. gangue, chiefly barytes and schist,† and is roasted in heaps several times. After roasting, the fines (which alone are lixiviated, the lump ore being smelted direct) contain ZnO 28 per cent., PbO 10 per cent., Fe_2O_3 13½ per cent., CuO 0·9 per cent., $BaSO_4$ 24 per cent., CaO, MgO, and Al_2O_3 5 per cent., and SO_3 16 per cent. They are charged, 1 ton or more at a time, into revolving cylinders or drums 4 feet long and 3 feet diameter, made of boiler plate with cast-iron ends, and there leached three or four times. The first two washings are with still hot weak liquors from a previous charge, and when drawn off they have densities of 50° B. and 20° B. respectively; two further washings are then given with hot water.

The first two washings are heated to boiling and allowed to stand for a week in large lead-lined pans; after which time almost all the iron has crystallised out as a basic salt, together with much gypsum. The clear liquors are concentrated in boiling pans to 50° B., and either drawn off to crystallisers, in which the zinc sulphate separates out, or to tanks in which they are precipitated with barium sulphide, obtained by reducing the barytes, which is a common gangue in the district. A double decomposition results with formation of two insoluble precipitates —viz., zinc sulphide and barium sulphate. The mixture is run through filter presses, dried, calcined, and, after grinding, is sold as a white pigment of fair covering power under the name of "lithopon."

A modification of this process for preparing a mixed white pigment is that of Cowley,‡ according to which ½ to 1½ per cent. each of freshly prepared magnesia and finely pulverised salt are added to the mixed precipitate sludge before filtration. The dried precipitate is further mixed with 3 per cent. of ammonium chloride before ignition or calcination. The colour prepared in

* *v.* Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 327; also Kerl in *Min. Ind.*, vol iv., 1895, p. 83.

† For details *v.* Table XIX., No. 4, p. 125.

‡ *Chem. News*, 1891, pp. 63 and 68.

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this way does not darken after long exposure to sunlight or to sulphuretted gases.

2. **The Parnell Process.**—This ingenious process was in operation at Llansamlet, near Swansea, from 1879 to 1883, but was commercially unsuccessful, owing, however, in part to causes quite independent of its merits. It comprised the following operations:—(1) Roasting at a dull red heat; (2) leaching with water to dissolve $ZnSO_4$; (3) heating in revolving lead-lined cast-iron pans with chamber sulphuric acid to dissolve ZnO; (4) leaching again with water to dissolve out $ZnSO_4$; (5) mixing the sulphate solutions and passing over scrap iron to precipitate any copper present; (6) evaporating to a paste, and stirring in powdered blende in the proportion of one-fifth by weight of the $ZnSO_4$; and (7) calcining in a muffle, whereby the following reaction took place—

$$3ZnSO_4 + ZnS = 4ZnO + 4SO_2.$$

The ZnO was sold to zinc smelters, the SO_2 from the muffle calciner, together with that from the ore roaster, was passed into lead chambers and converted into sulphuric acid. The leached residue after drying formed a readily saleable lead-silver concentrate sold to smelters. The losses of lead and silver are supposed to have been about 4 per cent., and that of zinc about 20 per cent. of the assay values.

The modification of this process, patented by Myalls and Wyatt,* consists in dividing the mixed solution from the water and sulphuric acid leaches into three-fourths, which are evaporated to dryness, yielding zinc sulphate; and one-fourth, in which the zinc is precipitated by means of alkaline sulphide. The sulphate and sulphide are then mixed and heated in a muffle.

3. **The Ashcroft Zinc Oxide Process.**—This process proposes to leach out the roasted ore with sulphuric acid as usual, to concentrate the zinc sulphate solution down to about 200 grms. Zn per litre, and then to add to it (instead of zinc sulphide, as in the Parnell and Wyatt processes) ZnO, in the proportion of two and a-half parts ZnO to one part $ZnSO_4$ present. This produces a basic zinc sulphate which is easily dried, and which is then heated in Hasenclever or other muffle furnaces to a full red heat, when it decomposes, yielding SO_3 and SO_2 in a highly concentrated form, which pass to lead chambers for conversion into H_2SO_4. Of the zinc oxide produced, one-third only is available for sale, the remaining two-thirds going back to form basic salt with a fresh portion of zinc sulphate. The large amount of material which has to be re-treated forms the principal drawback to this neat process.

* *Min. Ind.*, vol. iii., p. 432.

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4. **The West Process.***—Several hundred tons of mixed sulphide ores were treated by this process during 1889-90 at Thomasville, N.C.; but although the recovery of precious metals was practically complete, and the losses of lead and zinc only 20 per cent. and 30 per cent. respectively, the process was not a success under the conditions prevailing, which included an experimental and improved plant not well suited to the process. The following was the sequence of operations—(1) Roasting in a reverberatory; (2) cooling and wetting down, charging into false-bottomed tanks upon a layer of pebbles; (3) forcing the gases from the roasting furnace, together with a jet of steam, through the ore in the tank by means of a powerful blower for from six to twelve hours, by which means the zinc oxide present was eventually changed into sulphate; (4) removing the ore to leaching vats and leaching with water; (5) precipitating the zinc from the neutral solution as hydrate by means of gaseous ammonia generated in stills by the action of caustic lime upon ammonium sulphate; and (6) regenerating the ammonia from the solution after precipitation of the zinc, by heating it with lime in the stills aforesaid.

The leached residue, containing all the precious metals and practically all the lead and iron of the original ore, was dried above the roasting furnace, and was then sold to lead smelters.

5. **The Storer Process.**—This ingenious process, which it was proposed to employ at the Illawarra Works of the Smelting Company of Australia, consists briefly in roasting, leaching out the zinc sulphate with dilute acid, peroxidising any iron present, filtering and then precipitating the zinc by means of calcined magnesite as a hydrate, which is run through a filter press and then calcined to oxide. The magnesium sulphate mother liquors are evaporated to dryness and calcined at a red heat, regenerating magnesia, which is used over again for precipitating another tankful of zinc sulphate solution. The sulphuric acid vapours given off from the calcining furnace are condensed and used for leaching out the roasted ore, thus making the process regenerative, both as to solvent and precipitant.

6. **The Schnabel Process.**†—This involves roasting the ore at a cherry-red heat, with the object of converting the zinc into oxide, which is then dissolved by a solution of ammonium carbonate. It has never been tried on a commercial scale, and could not, I think, be made to pay on account of the cost of the plant, and of the manipulations necessary.

Other processes based upon the sulphatisation of the zinc and its removal are those of Croselmire ‡ and Emmens. §

* *Abs. Proc. Inst. Civ. Eng.*, vol. civ., p. 407.

† *v.* Chap. xvii., where it is described as employed for the treatment of zinc crusts; also Schnabel, *Handb. der Metallhüttenkunde*, vol. i., p. 564.

‡ *E. and M. J.*, Sept. 29, 1888; Feb. 9, 1889. § *Min. Ind.*, vol. iii., p. 431.

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7. **The Spence process**, unlike the foregoing, aimed at the separation of the lead, leaving the blende unaltered, together with the precious metals. It consisted in acting upon the finely powdered raw ore with hydrochloric acid, which dissolves galena before it attacks blende. The lead chloride was dissolved out by hot water and the lead precipitated from it by calcium carbonate, while the lead-free blende (carrying still all the precious metal contents of the ore) was roasted and distilled for zinc in the ordinary way, the residues being returned to the silver smelters. This process was worked for some years by the late Mr. Spence, but proved unsuccessful commercially.

C. ELECTROLYTIC METHODS.

1. **The Létrange process** consists in roasting the ore and leaching it with sulphurous acid, obtained by passing the furnace gases through water. The solution, containing zinc sulphite and sulphate, passes to tanks in which it is electrolysed, regenerating free sulphuric acid, which is applied to the leaching of another charge of ore until accumulated lime, iron, and other impurities render it necessary to start again with clean water. Practical difficulties in the electrolysis of acid zinc sulphate solutions prevented the process from attaining even technical success.

2. In the **Siemens & Halske process** the ore is roasted and leached with dilute sulphuric acid to obtain a sulphate solution for electrolysis. The liberation of free sulphuric acid, which proved fatal to the Létrange process, is overcome by Messrs. Siemens and Halske by the addition of ferrous sulphate to the electrolyte. This substance takes up oxygen as fast as it is liberated by the electric current at the anodes, producing ferric oxide which again combines with the sulphuric acid set free to form ferric sulphate, the combining power of iron for sulphuric acid being 50 per cent. greater in the ferric than in the ferrous condition. The solution of ferric sulphate then passes forward to the leaching tanks, where it dissolves more zinc, acting not only upon the oxide of that metal, but also to some extent upon unaltered sulphide; iron in the solution being partly precipitated in the interstices of the leaching charge and partly reduced again to ferrous sulphate, for which purpose, however, a certain amount of iron pyrites in the ore is found to be very desirable, if not, indeed, absolutely necessary.

3. **The Ashcroft Process.***—The difficulties met with in producing a coherent deposit by electrolysis of a zinc sulphate solution led this inventor to adopt in his original process, both at Broken Hill and at Grays, Essex, a chloride solution produced

* *Private notes*, 1896; also Threlfall, *Australian Mining Standard*, Jan. 20, 1897, and Ashcroft, *Trans. Inst. of Mining and Metallurgy*, vol. vi., pp. 282-337.

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by leaching the roasted ore with a solution of ferric chloride containing 10 grains of iron per litre, when the following reaction took place :—

$$3ZnO + Fe_2Cl_6 + 3H_2O = 3ZnCl_2 + Fe_2(HO)_6.$$

Besides the zinc, however, some iron, manganese, and silver always went into solution as well as lead, unless sufficient sodium sulphate were added to convert it into insoluble sulphate ; while part of the iron was reduced only to the condition of $FeCl_2$.

In the solution from the leaching vats any excess of Fe_2Cl_6 was first precipitated by addition of a little ZnO, and the solution was then pumped through filter presses to separate the residual siliceous matter of the ore, together with lead sulphate and the precipitated ferric hydrate. The cakes from the filter presses were broken up and briquetted, for smelting with lead concentrates and other ores.

Traces of lead, silver, copper, arsenic, and antimony in the solution were separated by agitation with "zinc grey" (blue powder), and the purified solution passed to the electrolysing vats (Fig. 108). In these it was found impossible to use carbon anodes owing to the accumulation of free acid which produced a loose, mossy deposit containing much occluded hydrogen; as well as on account of their rapid disintegration by the free chlorine evolved ; it was, therefore, necessary to employ iron anodes in order to take up the free acid liberated. As one equivalent of iron must go into solution for each equivalent of zinc deposited, the cost was very heavy ; though the iron dissolved was all reprecipitated in the interstices of the ore during the leaching process and was so rendered available as a flux for the excess of siliceous material. In order to prevent the presence of iron round the cathodes, which interfered with the deposition of zinc, canvas diaphragms were introduced into the cells through which the electro-

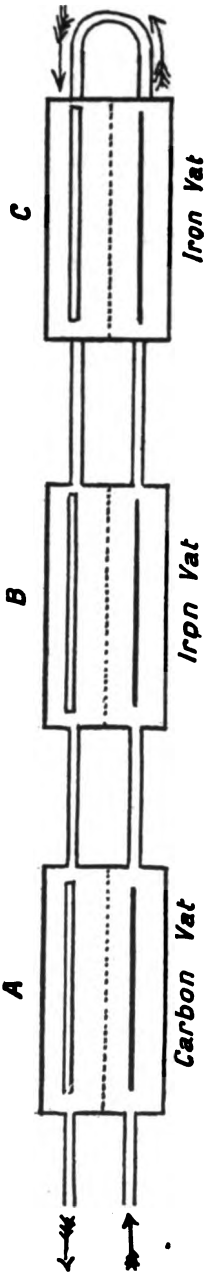

Fig. 108.—Electrolysing Vats.

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lyte was circulated so as to separate the liquid in which the iron anode plates were being dissolved from that surrounding the cathodes upon which zinc was being deposited. If all the vats had contained iron anodes, however, all the iron dissolved in the electrolyte would have taken the condition of ferrous chloride, in which form it would have been useless for leaching, so that a sufficient proportion (about one-third) of the cells were provided with carbon anodes in order to insure that the whole of the iron in the electrolyte should be in the ferric condition, and in this way the consumption of iron could be reduced to two-thirds of an equivalent per equivalent of zinc deposited. It was found that a hard and firm deposit of zinc from a chloride solution could only be obtained when the electrolyte was circulated *rapidly*, and when instead of being acid it was slightly *basic*, this latter condition being insured by the addition of a little zinc oxide in the storage vats.

In working on a large scale the ferric chloride liquor was found to be quite unmanageable, corroding rapidly any form of metallic pump, and owing to this and to other causes a reversion was made at the *Cockle Creek* Works to the use of sulphate solutions, which could be readily handled with centrifugal pumps made of hard antimonial lead. With sulphate solutions the carbon anodes have to be replaced by lead plates which last twelve months, being then converted largely into peroxide. With this change it was finally found practicable to dispense with the iron anodes and their accompanying consumption of that metal and to use lead anodes exclusively, by which means an acid solution was regenerated for leaching, containing free H_2SO_4 instead of Fe_2Cl_6, the diaphragms in the cells preventing this free acid from interfering with regular deposition on the cathodes.

The principal difficulties met with in the operation of this modified process on B.H. ores at the Cockle Creek Works* were the following:—

1. Difficulty of roasting even a very fine material so as to produce any sulphate of zinc whatever, all the sulphuric acid produced being generally insufficient to convert the whole of the lead present into sulphate; and the consequent necessity of providing sulphuric acid from other sources for leaching.

2. Impossibility of leaching thoroughly by percolation, which rendered it necessary to adopt the costly processes of agitation and filtering in presses. Even in filter presses, however, unless the solutions are at a temperature of 80° C. or over, and unless the free acid contained is kept below 100 grains per litre, it is very difficult to filter the ore-mud owing to separation of gelatinous silica.

* Ashcroft, *Trans. Inst. of Mining and Metallurgy*, vol. vi., p. 282, *et. seq.*

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3. Gradual accumulation of manganese in the solution, which not only interfered with the solution and deposition of zinc, but used up a large amount of sulphuric acid, since a portion of the solution had to be periodically run to waste or treated by some other process for recovery of the zinc contents in order to keep the accumulation of manganese within bounds.

4. Difficulty of maintaining the electrolyte in such condition as to produce a uniformly hard and coherent deposit. It seems to be proved that not only the presence of traces of lead, antimony, arsenic, and other metals, but also traces of organic matter from new vats, oil from the re-use of condensed exhaust steam in the boilers supplying live steam for boiling up the leaching vats, and other, as yet unexplained, conditions will instantly change the character of the deposit from a hard, coherent, mass, like electrolytic copper, to mossy arborescent growths, or even to a black spongy mud which is practically valueless.

5. Difficulty of smelting the filter press cakes containing the lead and siliceous matter of the original ore, together with 8 per cent. of residual zinc without previous briquetting and drying, and the necessity of adding a very large amount of flux, now that, owing to the abandonment of iron anodes, there is no longer any addition from outside to compensate for the iron and manganese dissolved out from the ore in leaching.

Owing to these difficulties, and to the cost of the various manipulations required, the process has been abandoned, though its inventor is still of opinion that on a very large scale it could be made a commercial success. The plant required, however, is very complicated, and for a capacity of 1000 tons of ore per week no less than £250,000 must be expended; it is highly improbable, therefore, that in its present form the process will come into use as a solution of the so-called "sulphide problem."

D. NEW DRY PROCESSES.

A process has been recently patented by Greenway which aims at the elimination of practically all the lead and silver contents of the "zinc-lead middlings," containing 25 to 35 per cent. zinc, by roasting with salt at a low heat. The lead and silver are converted into volatile chlorides which can be condensed by suitable means, and the half-roasted residues, after leaching to remove sodium sulphate, are raised to from 35 to 50 per cent. zinc, in which condition they are eminently suitable for distillation.

It is possible that this method may prove to be a successful one for dealing with these hitherto very intractable middlings which contain, besides silica and felspar, such large quantities of garnet and rhodonite mixed with the blende as to render them too poor for treatment in their present condition.

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In view, however, of the great success of the Wetherill magnetic concentrator in removing just such slightly magnetic material as garnet and franklinite from non-magnetic ores of zinc and copper, it seems to the author very probable that passage through such magnetic separators might remove, at trifling cost, such a large amount of ferruginous and manganiferous material as to raise the percentage of zinc in the residue by just the 15 or 20 per cent. which is necessary in order to make it a valuable ore of zinc capable of being shipped under existing conditions to European zinc works at a considerable profit. This would have the further advantage of raising the percentages of lead and silver in exactly the same proportion with the percentage of zinc so that the residues from zinc distillation would be proportionately more valuable for smelting.

Seeing that the material is accumulating at Broken Hill at the rate of 15,000 tons per week, there is great scope for the introduction of such comparatively cheap methods of dry concentration as that here suggested, at all events for the zinc-lead middlings. There would seem to be no doubt that wet concentration must always be the first step in the treatment of Broken Hill ores so as to separate as much lead as possible in an easily realisable form, and the production of these zinc-lead middlings is a necessary evil of the wet concentration process. The practical field for experiment, therefore, is confined to endeavours in the direction of economical extraction of the zinc, lead, and silver locked up in these middlings.

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SECTION III.—DESILVERISATION.

INTRODUCTORY.

The distinction between argentiferous and non-argentiferous lead ores has been already emphasised (Chapter ii.); as also the fact that the latter are usually much purer and more free from base metals. Thus the lead obtained from Missouri and Wisconsin lead ores (as also a part of that from Spain and Germany) is comparatively free from silver, as well as from base metals, and can, therefore, be manufactured almost as it leaves the smelting furnace after a simple "poling," or at most a few minutes "blowing" with a steam jet. All the lead produced in blast furnaces from complex ores, however, as well as a large part of that produced in reverberatories, contains at least sufficient silver to pay for its extraction, even if, indeed, the silver contents be not more valuable than the lead itself, as in the case of Freiberg, Colorado, and Broken Hill ores.

Classification of Methods.—The desilverisation of lead bullion may be performed by three different methods—viz., 1, Cupellation; 2, the Pattinson process; and 3, the Parkes process. The first method, though the simplest, is the most expensive for labour and the most wasteful of material; yet it may still be adopted with advantage, in spite of its high losses, for the treatment of *rich* lead in very inaccessible districts where the silver is really the valuable metal sought, and lead (owing to the heavy freight) almost valueless. Such conditions prevail in some parts of Mexico and in the mountainous districts of S. America and elsewhere. In such cases it is sometimes advisable to adopt a direct cupellation process, which turns out the silver at once in a portable form, while the litharge is either reduced to metal in an open hearth or simple furnace, or, more commonly, is utilised as a source of lead in smelting silver ores.

Direct cupellation has the advantage that it can be carried out, if necessary, with no other material than clay or sun-dried bricks, no other fuel than brushwood, and no other blowing machinery than a common blacksmith's bellows. For further information as to simple cupellation hearths, two papers by Austin,* and one by Pfordte† may be consulted with advantage.

* *Trans. A.I.M.E.*, vol. xii., p. 41, and xiii., p. 185. † *Id.*, vol. xxi.

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In all cases, however, where fuel is cheap and the country moderately accessible by means of railways or good roads, the direct cupellation process should be replaced by either the Pattinson or the Parkes process. An example of a case where this was not done is afforded by the Las Trojes smelting works in Michoacan, Mexico,* which the author understands are no longer in operation. Hofman quotes† from Reich the following table which shows at a glance the comparative disadvantages of cupellation as compared with the Pattinson and Parkes processes, and is, therefore, worth reproduction. The figures are from the Ems works, where all three processes were carried out successively.

	Cupellation.	Pattinson.	Parkes.
Cost of treatment per ton, . .	3	1½	1
Amount of lead to be cupelled, . .	100	13	5
Percentage recovery of lead and silver,	94	98	99
Silver lost in the lead, ozs. per ton, .	0·73	0·58	0·17
Traces of gold, ...	lost	lost	recovered

Electrolytic processes of desilverisation were tried experimentally by Hampe‡ and Keith;§ but, though technically successful as regards the purity of the resulting lead and its freedom from silver, they have been failures from a commercial point of view, the chief drawbacks being—(1) enormous amount of capital locked up in material under treatment; (2) inconvenient condition of the fine crystallised lead produced, which gives rise to heavy losses in remelting, &c.; (3) losses in melting and treating the slimy residue containing the precious metals. Recently, a new process has been patented by Tommasi,‖ the electrolyte being a double acetate of lead and sodium, and the cathode a disc which is made to revolve, upon the surface of which the crystals of lead are deposited. These are removed at intervals by scrapers, and well washed on a sieve. The wash water is concentrated by evaporation and added to the bath, while the lead is compressed into blocks and then melted in crucibles with 2 per cent. or 3 per cent. of charcoal, and cast into ingots. It remains to be seen whether this process will be any more successful than those of previous experimenters in the same field.

Practically speaking, therefore, the desilverisation of lead must be carried out on the large scale by either the Pattinson or

* *Proc. Inst. Civ. Eng.*, vol. cxii., pp. 146, *et seq.*; 165, *et seq.*

† *Metallurgy of Lead*, 1893, p. 297.

‡ *Zeitschrift f. d. Berg- Hütten- u. Salinen Wesen. im Preuss. Staate*, 1882, p. 81.

§ *Trans. A.I.M.E.*, vol. xiii., p. 310.

‖ *Comptes Rendus*, vol. cxxii., p. 1476; and *E. and M. J.*, Aug. 29, 1896.

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the Parkes process. Both are English processes, and both have been brought to their highest state of perfection in this country, but unfortunately the traditions of English smelters and refiners have always led them to keep their operations as secret as possible, even in cases where their foreign competitors have already copied all that is worth copying;* therefore, few particulars are available as to English practice, and hence the descriptions of plant, &c., must be mostly drawn from foreign localities.

Influence of Impurities on Desilverisation.—Almost all the impurities in the work-lead interfere, to a greater or less extent, with desilverisation by either process, although, generally speaking, the Parkes process requires a purer lead than the Pattinson.

The most harmful impurity is *arsenic*, which, even in small proportion, is fatal to good results; *antimony* also, even in small quantity, interferes greatly with the Pattinson process, and renders good work in the Parkes process impossible. Next in order among harmful impurities come *tin*, *zinc*, *sulphur*, *iron*, *nickel*, and *cobalt*. Fortunately, all the above have a greater affinity than lead for oxygen, and can, therefore, be eliminated by simple oxidation at a low red heat and skimming the molten bath.

Copper, which is, perhaps, as common an impurity as any of the above, has much less affinity for oxygen and is only imperfectly got rid of by oxidising influences. It forms, however, with part of the lead itself an alloy which is much less fusible than the remaining and purer lead, and, therefore, the bulk of it can be readily eliminated by means of a process of liquation or slow melting down, a smaller proportion, by subsequent cooling, gradually rising to the top as a second crust or dross, which can be skimmed off. The first dross, besides copper, contains also most of the metals of the iron group contained in the lead, as well as some arsenic, sulphur, and tellurium, if present.† Copper is not specially harmful in the Pattinson process, but greatly interferes with the Parkes process, increasing the time and the consumption of zinc.

Bismuth has distinctly less affinity for oxygen than lead itself, and cannot be readily separated from it; fortunately, this metal does not interfere at all with desilverisation, even in the proportion of 2 per cent., as shown by the experience at Freiberg. *Zinc* is a rare impurity in work-lead, except in minute traces, but

* An amusing commentary on this condition of affairs is to be found in the concluding remarks of the presidential address of Dr. R. Pearce (himself an Englishman and a pupil of Dr. Percy) to the American Inst. of Mining Engineers in June, 1889. *Trans. A.I.M.E.*, vol. xviii., p. 72.

† Tellurium is found in notable quantity in the dross from base bullion produced at Pertusola (Italy). *v.* Heberlein, *Berg- u. Hüttenm. Zeitung*, 1895, p. 41.

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is contained in considerable quantity in lead which has been desilverised by the Parkes process, and must be got rid of by oxidation before the desilverised lead is marketable.

The process of desilverisation adopted must, therefore, be preceded by a process of oxidation to remove impurities, which is called "softening," or, sometimes in England, "improving"; while the Parkes process is followed by another similar oxidation to remove zinc, which is usually called "refining," or, sometimes, "dezincing." Both operations require similar plant, and may be conveniently described together in a single chapter. The concentration of precious metals in rich lead by the Pattinson and Parkes processes follows in two separate chapters, and, lastly, the cupellation of the rich lead and refining of the silver.

As an alternative to the combined softening and desilverisation by ordinary methods, Rösing* experimented at Tarnowitz (Silesia) on a Bessemerising process in a converter, with basic lining, taking charges of 6½ tons. By this means lead containing 12·4 ozs. silver was almost entirely converted into a fume containing 75 per cent. lead and 2·4 ozs. silver per ton, the residual rich lead carrying 1863 ozs. to the ton. The author has not succeeded in learning any later particulars as to the practical working of this process, but the losses of lead and silver consequent on the re-treatment of so large a quantity of flue dust would seem to be a fatal objection.

CHAPTER XV.

SOFTENING AND REFINING FOR MARKET.

THE softening of lead as a preliminary to desilverisation may take place in cast-iron kettles or in reverberatory furnaces. The former are suitable for softening lead practically free from antimony and arsenic, and containing only small proportions of copper. The latter are much more commonly employed, since they are adapted to the softening of more impure lead, containing larger quantities of copper, arsenic, and antimony. When lead contains ¾ per cent. of copper and upwards, as at Freiberg and Przibram, it is advisable to preface the ordinary softening process by liquation in a special liquation furnace with inclined bed, the lead gradually draining out into a kettle, from which it can be tapped or syphoned into the softening furnace. In any case, the rapidity with which softening proceeds depends on the exposure of fresh surfaces to oxidation.

* *E. and M. J.*, April, 16, 1892.

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Refining, like softening, may be carried out either in kettles or in reverberatories. In the former, steam is the active agent (Cordurié's process); in the latter, atmospheric oxidation is exclusively relied upon, the process being slower and, perhaps, less thorough, but on the whole less costly.

Softening in Kettles.—At *Lautenthal* (Upper Harz) * the

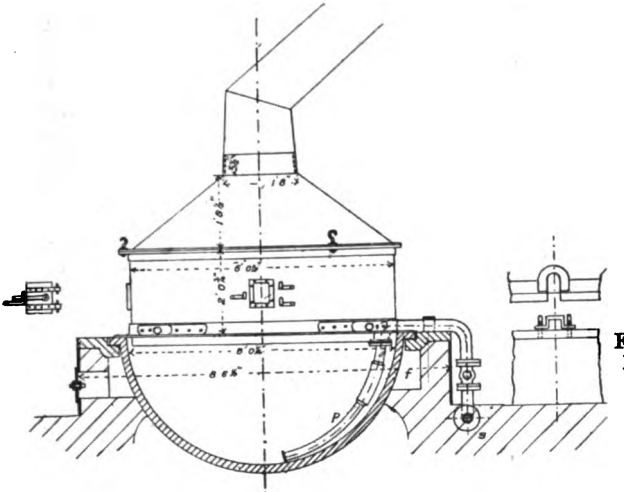

Fig. 109.

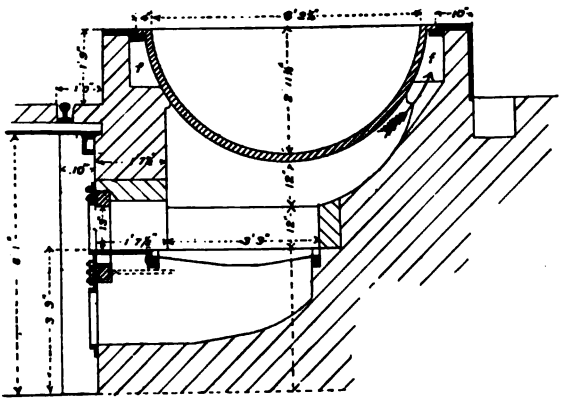

Fig. 110.

Figs. 109 and 110.—Kettle.

* Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., pp. 451, *et seq.*

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softening, desilverisation, and subsequent refining are all conducted successively in the same kettle. Analyses of the work-lead treated are given in Table XXXIII.; it is comparatively free from arsenic and copper, and not very high in antimony. The kettles used are 6 feet $2\frac{3}{4}$ inches (1·90 m.) diameter by 2 feet $11\frac{3}{8}$ inches (0·90 m.) deep, and hold about 15 tons of lead each; their arrangement is shown in Figs. 109 and 110. The lower part of the kettle is heated directly by the flame, which then rises through the opening shown by the arrow and circulates round the upper part of the kettle in the flue, *f*, before passing, by a downcast, to the principal chimney flue. The hood and steam apparatus shown in Fig. 109 is not used for softening, but only for refining, for which purpose also a removable cast-iron pipe, *p*, hangs in the kettle and can be connected at will by means of a valve with the steam pipe, *s*.

Softening.—The charge of 15 tons of lead (containing 0·28 per cent. Cu and 0·57 per cent. Sb) is slowly melted down at a low temperature, taking six hours, at the end of which time two-thirds of the copper, together with all the sulphur and one-half of the arsenic, iron, and nickel will have risen to the surface as a pasty "dross," which is skimmed off, leaving, however, practically all the antimony behind alloyed with the lead. A sample of the lead at this point poured into a mould shows, on cooling, a bright white crystalline spot in the centre of its dull greyish white surface, which is an infallible indication of the presence of antimony or arsenic.

The desilverisation with zinc follows, lasting fifteen hours and removing most of the remaining copper, without, however, affecting the antimony.

Refining.—The cooled desilverised lead, now containing 0·7 per cent. of zinc as well as the original 0·57 per cent. Sb, is then heated to a dull red by four hours' strong firing, the hood lowered to prevent access of air as far as possible, and steam at 30 to 40 lbs. pressure blown through the bath to oxidise the zinc. It is impossible to prevent the introduction of air along with the steam, and therefore some lead and antimony are oxidised together with the zinc. The expulsion of zinc generally takes about two hours, at the end of which time the hood is raised and the oxides skimmed off. The hood is again lowered, its four working doors are opened and steam is blown through with free access of air to oxidise the antimony, with formation of a thick semi-fluid mass of lead antimoniate. This also takes about two hours, when fluid yellow feather-litharge begins to form showing the antimony to be practically all expelled; after cooling, the lead is then cast into moulds by means of the Rösing lead pump.*

The yellow powder of zinc and lead oxides is separated by hand buddling from the shots of lead, and the most impalpable

* *Berg- und Hüttenmännische Zeitung*, 1889, p. 262.

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part of it, which floats away, forms, after drying, a good reddish-yellow paint containing 60 to 67 per cent. ZnO, the remainder being practically all PbO. In order to avoid so much oxidation of lead, Rössler* has forced in, together with the steam, CO_2, which yields a nearly pure zinc oxide; also a mixture of CO and nitrogen, which yields a considerable proportion of the zinc as "blue powder"—*i.e.*, in the metallic condition. The improvement has not, however, come into general use.

The great drawback of kettle refining is the wear and tear of the kettles, which are rapidly corroded away at the surface of the metallic bath by the lead antimoniate. At *Lautenthal*, cast-iron kettles only last for 20 to 40 charges; at *Tarnowitz*, with a lead almost free from antimony, cast-iron kettles last for 90 charges; while those of open hearth steel last 120 to 150 charges; and those of crucible steel 250 to 270 charges. Whatever their material, kettles for these other purposes should always be cast bottom downwards, though the other way up is easier for the foundry.

At *Hoboken* (Antwerp) Spanish lead is treated by this process, no attempt being made to separate the zinc and antimony, which are recovered together in one product for further treatment.

Liquation of Cupriferous Lead.—At *Freiberg*† the work-lead containing 0·9 per cent. copper and other impurities (*v.* analysis in Table XXXIII.) is liquated, together with all the skimmings from the subsequent Pattinsonisation, on the hearth of a special furnace very similar to that shown in Fig. 131 (Chap. xvii.). The pigs are piled on an inclined hearth of marl, and gently heated by means of the flame from a closed grate supplied with blast under the bars so as to burn inferior slack coal. The lead trickles out and collects in a pot, from which it is tapped from time to time through a spout. In twelve hours 12 tons of base work-lead are slowly melted down in the above furnace with a consumption of about 2 tons of slack coal; and from 4 to 5 per cent. of residues remain upon the hearth containing practically all the sulphur, 93 per cent. of the copper, 96 per cent. of the nickel and cobalt, 77 per cent. of the iron, and 25 per cent. of the arsenic of the original lead, which, however, retains all its original bismuth, all its tin but 1 per cent., and all its antimony save about $5\frac{1}{2}$ per cent. The dross melted down and allowed to cool separates into three separate products—viz., lead, speiss, and matte.‡ The comparative absence of iron from the two latter, however, proves that they are not original furnace products held in suspension by the lead, but that the natural affinities of S for Cu and of As for Ni, Cu, and Pb come into operation to form compounds less fusible than the lead, which

* *Ibid.*, 1890, p. 248.

† Schertel, *Berg- u. Hüttenmännische Zeitung*, 1882, p. 293. ‡ *Ibid.*

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dissolved them in the smelting furnace at a much higher temperature.

Neither at *Freiberg* nor at *Przibram* is the liquated lead sufficiently pure to be passed on to the Pattinson process without further softening, most modern works, however, treat lead less cupriferous than that mentioned above, so that it is possible to purify it sufficiently for desilverisation in a single furnace with great saving of time and fuel. Still, at the *Broken Hill* Works, it has been found very advantageous to employ a system of two separate, but similar, furnaces for drossing and softening, as will be described hereafter.

TABLE XXXIII.—ANALYSES OF WORK-LEAD BEFORE AND AFTER LIQUATION.

	Lautenthal.		Freiberg.		
	Before Drossing.	After Drossing.	Before Drossing.	After Drossing.	Liquated Dross (5 %).
Pb, . .	98·96475	99·1883	96·667	97·830	62·40
Ag, . .	0·1413	0·1440	0·549	0·536	0·17
Cu, . .	0·2838	0·0907	0·940	0·042	17·97
Cd, . .	tr.	none	...	...	...
Bi, . .	0·0082	0·0083	0·066	0·066	none
Sb, . .	0·5743	0·5554	0·820	0·771	0·98
As, . .	0·0074	0·0032	0·449	0·333	2·32
Sn, . .	none	none	0·212	0·210	0·04
Fe, . .	0·0089	0·0048	0·027	0·006	0·43
Zn, . .	0·0024	0·0015	0·022	0·021	0·07
Ni, . .	0·0068	0·0038	} 0·055	0·001	1·09
Co, . .	0·00035	tr.			
S, . .	...	...	0·200	0·180	4·00
O, . .	...	...	...	...	1·87
Slags, &c., .	...	...	...	...	8·66

References.—1 and 2. Hampe, *Zeitschr. f. B. H. u. S. W. im Preussen*, vol. xviii., p. 203. 3 and 5. Schertel, *B- u. H. Zeitung*, 1882, p. 293. 4. By difference from 3 and 5.

Softening in Reverberatories.—The operation consists of two stages—viz., drossing and oxidation; the former is a liquation which takes place during melting down, the dross which rises to the surface containing most of the copper. The temperature is then raised to cherry red, and with free access of air tin, arsenic, and antimony oxidise successively, and are removed by skimming.

In Germany and at a majority of old works in England, softening furnaces are still used, in which the hearth is only

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cooled by radiation through the cast-iron foundation pan, while at Freiberg and Przibram oxidation is accelerated by means of an air blast.

At *Freiberg* the charge is 21 tons, which takes thirty-six hours to soften completely, and yields 85 per cent. by weight of softened lead. Three kinds of skimmings are taken off, which are sometimes divided into six classes as one variety runs into the next. The first skimmings after the melting down are of a dark yellow colour, contain most of the tin, and are, on that account, powdery. They consist mostly of antimoniate of tin and stannate of lead, but as oxidation proceeds antimoniates and arseniates of lead are found and the skimmings become pasty. All these skimmings (*abstrich*) are drawn near the door nearest the flue and are called "tin skimmings." Fumes of arsenic and antimony then appear, and the former element (together with some of the latter) oxidises rapidly to a light brown arseniate of lead, which is drawn off with a long iron hoe having a wooden blade and called "arsenic skimmings." The brown arseniate of lead gradually gives place to the almost black antimoniate and the next lot of skimmings is called "antimony skimmings." As the antimony becomes eliminated the black is more and more replaced by greenish-yellow litharge.

So long as there is any perceptible amount of antimony in the lead, a sample in a ladle will show globules of black skimmings revolving on the unoxidised surface of the metal like grease on water; but when nearly all the antimony is "out" the globules are replaced by a uniform yellow coating of litharge which forms quickly. Poured into a mould and skimmed just before solidification the bar shows the characteristic even, smooth, blue surface and lustre of soft lead.

At *Przibram* the charge is 22 tons, which is softened in twenty-four hours with a consumption of 9 per cent. of coal, and yields 81 per cent. of its weight as softened lead.

At modern works in the United States and England, it is customary to use water-jacketed softening furnaces built into large wrought-iron pans in order to reduce the amount of corrosion of the walls by lead antimoniate and oxide, which is very serious in the case of unjacketed furnaces. Some furnaces have been built with two complete pans, having a 3 to 4 inches space between, filled with water; but the cooling effect is then very great and causes excessive consumption of fuel to soften the lead sufficiently quickly. The corrosion of the hearth is never very serious and air cooling is quite sufficient; while the corrosion of the walls when water jacketed is very easily repaired with common clay* or with brasque which is tamped in between charges.

*Common clay is much better than fireclay for almost all internal "patch" repairs of furnaces of every kind.

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Furnace Construction. — The construction of a 35-ton softening furnace at the *Port Pirie* Works of the *Broken Hill Proprietary Co.*, divested of its binders and water connections for simplicity, is shown in Figs. 111 to 115, in which *a* is the hearth separated from the firebox, *b*, by an air space beneath the bridge, which is supported by a massive casting as shown. The hearth is wholly enclosed in a tank of $\frac{5}{16}$-inch mild-steel plate, to the upper part of which is attached the mild-steel water

Fig. 112.

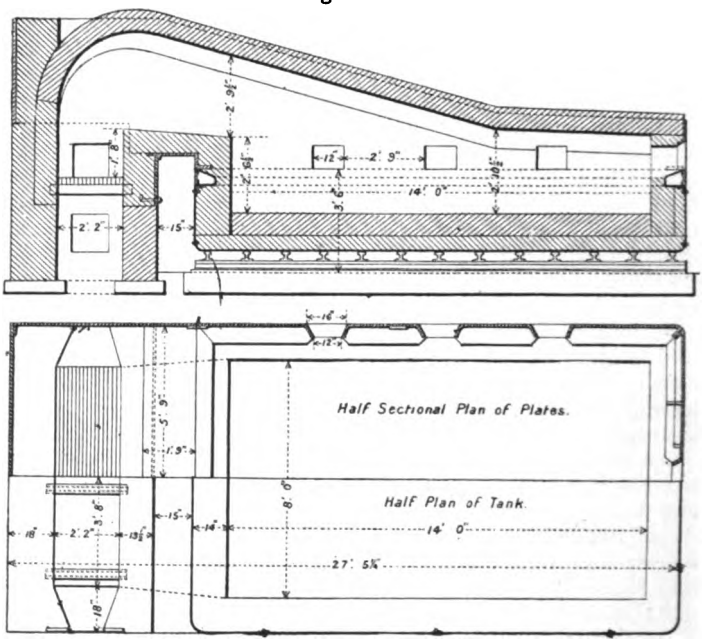

Fig. 111.

Figs. 111 and 112.—Port Pirie Softening Furnace.

jacket of wedge section, detail of which is given in Fig. 114. The tank containing the hearth is supported upon a layer of 80-lb. rails pretty close together, as shown. The water jacket has 1¼-inch water connections, and handholes here and there for cleaning. The position of the taphole is not shown, but Fig. 115 gives detail of the cast-steel tapping jacket, the taphole in which is closed by a screw plug. In some of the furnaces (the so-called "copper furnaces") the tapping jacket is placed at the side, while in others (the so-called "antimony furnaces") it is placed at the end, its exact position being determined by

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the most convenient arrangement of the works. The whole upper part of the furnace above the steel-plate tank is enclosed in a close fitting casing of massive cast-iron plates, of which

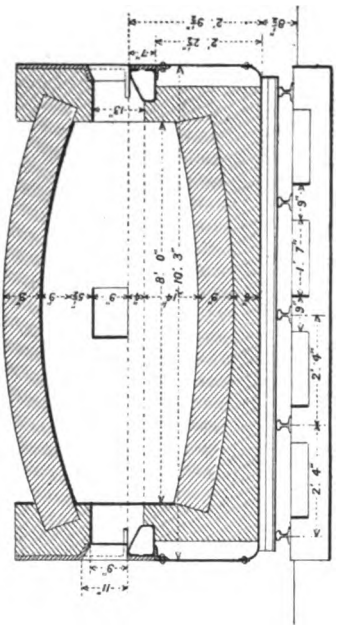

Fig. 113.

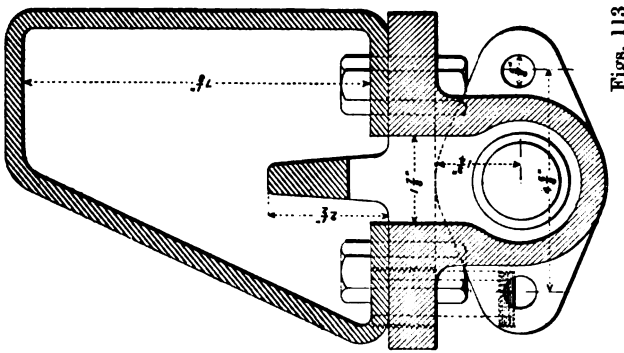

Fig. 114.

Figs. 113 and 114.—Port Pirie Softening Furnace.

the door frames form an integral part; and the furnace is also strongly braced with old rails and tie-rods to resist the expansion. The furnace gases pass through the opening into a

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horizontal flue, which crosses the end of the furnace and leads into an independent downtake for each furnace connected with the main underground flue of the refinery. There are three doors on each side of the furnace which serve for charging and skimming respectively, and one skimming door in the end opposite the firebox. The hearth is built of the best firebrick as an inverted arch, and must be laid with the closest possible fire-clay joints to make it lead tight; the working bottom is similarly built as shown in Fig. 113, and tightly wedged against its skewbacks in the side walls. Air is frequently admitted through the bridge and roof to accelerate oxidation, and sometimes also a blast is used under the grate when inferior slack is to be used as fuel.

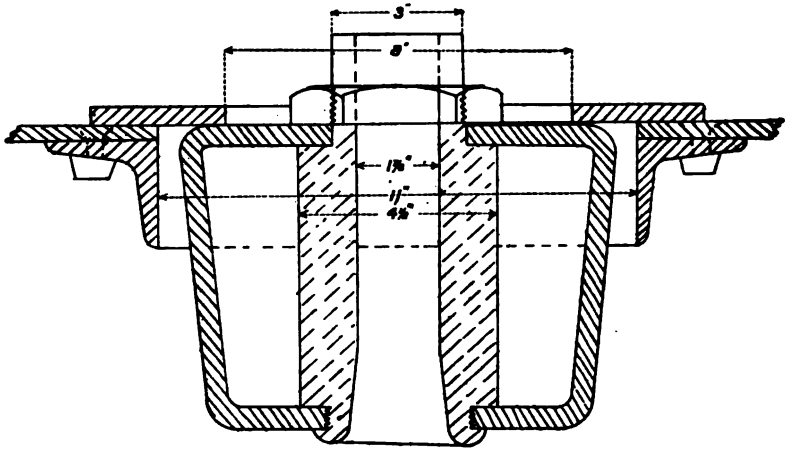

Fig. 115.—Port Pirie Softening Furnace.

American and English softening furnaces are very similar, except that in the latter a simple water pipe extending round the furnace inside the iron or steel tank is sometimes used instead of a jacket; and that in the former the water jacket is frequently a rectangular box, the inner side of which is formed simply by the side of the wrought-iron hearth tank, while the top and bottom are of square bar or of channel iron rivetted to it and to the outer plate. Figs. 116 to 119 represent an American softening furnace with rectangular water jacket, and end taphole passing through an extension of the wrought-iron jacket. Other details of the furnace are, in the main, similar to those of the Australian furnace previously figured.

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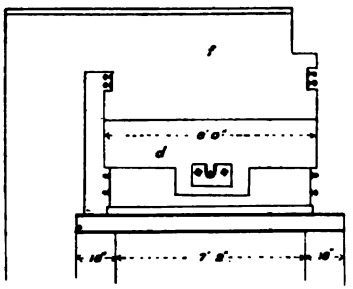

Fig. 116.

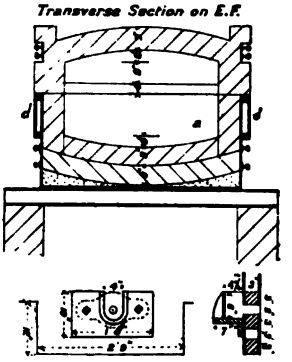

Fig. 117.

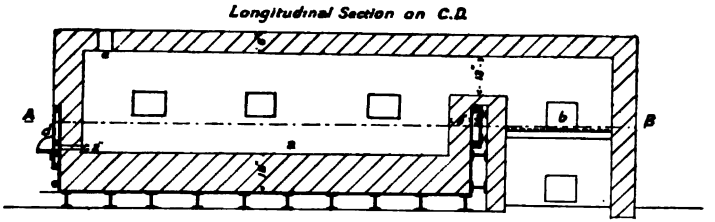

Fig. 118.

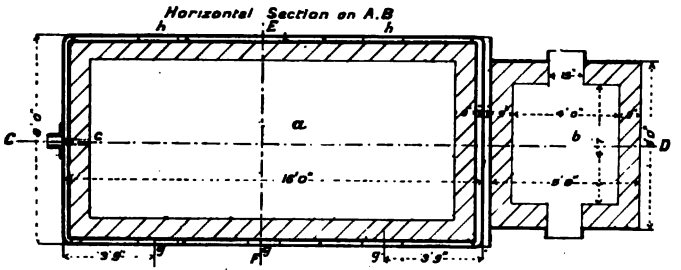

Fig. 119.

Figs. 116-119.—American Softening Furnace.

Method of Working.—The pigs of lead must be introduced carefully so as not to injure the working bottom, and within a period of from one and a-half to five hours after the charging is finished (according to the temperature employed) they are all melted and the dross ready for skimming. To assist in collecting the dross, a little fine coal is sometimes stirred in, and then the

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dross is all skimmed off by a rabble with long flat head resting in a hook suspended by a chain. The dross usually contains about 80 per cent. of lead, and averages in weight from 3 to 5 per cent. of the bullion charged; it is collected in slag pots or barrows, weighed, and wheeled to the liquation furnace. When the bullion has contained tin, the pasty tin skimmings are next removed in the same way as the dross. The antimony skimmings are more fluid, and, therefore, the furnace doors are frequently opened to cool them and permit of their more ready removal. Lime is sometimes thrown on to cool and thicken the mass, but this plan interferes with the subsequent liquation, and is, therefore, but seldom adopted. It is necessary to thoroughly stir the bath at frequent intervals, say at least every half-hour, for, otherwise, clean litharge would be shown, and the surface layer of lead become freed from antimony while that at the bottom was still very impure. Stirring and skimming must be repeated until the lead is found to be soft, as shown by the ladle test already described. The texture and appearance of the last skimmings, however, are not an invariably safe guide unless the whole be carefully examined, for a considerable portion of a skimming averaging 6 per cent. of antimony may show well developed flaky crystals of clean litharge, the antimony appearing to segregate in certain portions of a skimming.

To hasten the process, jets of steam have been sometimes introduced through perforated pipes. These, however, have the ill effect of increasing the oxidation of lead, and, consequently, the amount of skimmings produced; besides which the corrosion of the furnace walls is largely increased through the wave motion of the bath. By far the most efficacious method of hastening the removal of antimony is to stir litharge into the bath at a comparatively low temperature, particularly the very rich litharge from the finishing cupels and the second refining skimmings, which are very rich in metallic lead. This practice results in a considerable saving of time in oxidation, besides affording a very convenient means of disposing of these bye-products. The "softening skimmings" will vary in amount according to the impurity of the bullion; usually, however, they do not amount to more than 5 to 8 per cent. of the weight of base bullion charged.

The fuel usually employed is coal, the average consumption of which in America, according to Hofman, is 7½ per cent. by weight of bullion treated.* If this figure be correct, however, it should certainly not stand as a record of the best work, for the *Broken Hill Proprietary Company* at Port Pirie soften their very impure bullion in twenty-four hours with a consumption of only 5·2 per cent. of coal; while at the *Howdon* Works (Newcastle-on-Tyne)

* *Metallurgy of Lead*, 1893, p. 324.

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bullion with 3 per cent. impurities is softened in 140-ton furnaces with a coal consumption of only 2½ per cent. by weight.* Crude petroleum sprayed by a Körting injector, or, better, by a jet of compressed air is used in some American works with good results.

The average time taken to soften ordinary American lead bullion is fourteen hours. In the United States the usual charge is 30 to 40 tons (rarely 50 tons), and the lead softened thus quickly at a comparatively high temperature is run direct from the furnace into the zincage pots, an arrangement found also at some Continental and English works. Hutchings recommends† the use of much larger furnaces taking charges up to 140 tons and softening slowly at a lower temperature. By this method, even with work-lead containing 3 per cent. of impurities, taking forty-eight hours to soften, the fuel consumption is only about 2½ per cent. by weight, as compared with the American consumption of about 7½ per cent.; the saving in fuel being much more than the loss in interest. Hutchings further recommends casting the lead from the softening furnace and remelting it in the desilverising kettles as affording opportunity for an additional skimming of coppery dross, yielding a purer lead and saving zinc. The same object may, however, be attained by allowing the lead to cool off almost to the solidification point before heating up for the first zincing, or, as pointed out by Huntington,‡ by interposing a collecting pot between the softening furnace and desilverising pot in which this cooling and drossing takes place, bringing down the copper contents of the bullion to 0·08 per cent., even when originally containing as high as 0·45 per cent. The latter writer further points out that the 140-ton furnaces would be out of place in medium-sized works where the softening furnace forms only a part of one continuously working whole; though suitable enough for a desilverising plant, pure and simple, working on a sufficiently large scale.

At the *Port Pirie* refinery of the *Broken Hill Proprietary Company*, the average bullion treated contains 0·8 per cent. Cu, 0·7 per cent. Sb, 300 ozs. Ag, and 5 dwts. gold per ton (*v.* analysis, Table XXIII., p. 197). At these works two separate sets of furnaces are employed for drossing and softening respectively, the latter being built on a slightly lower level, about 1 foot below the former. There are two drossing furnaces arranged lengthwise on the uppermost level, each of which supplies a pair of softening furnaces of the same dimensions placed end on. All the furnaces are of the same type, and approximately of the same dimensions; they have been illustrated in Figs. 111 to 115.

The charge for a drossing or "copper" furnace is 35 tons (*i.e.*, of 2240 lbs. = 39·4 tons American), which takes about three

* Hutchings, *E. and M.J.*, Feb. 23, 1896.
† *E. and M. J.*, Feb. 23, 1895. ‡ *E. and M. J.*, Mar. 30, 1895.

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hours to charge in carefully with long paddles, so as not to injure the bottom. As the furnace is kept at a very low and uniform temperature, the charge takes four or five hours to melt down; as soon as this operation is completed the doors are thrown open so as to prevent it from getting any hotter, and the dross, which weighs about 3 tons after liquation, is skimmed off. The operations of melting and drossing take about five to six hours in all, or eight to nine hours from the time charging was commenced, and the consumption of coal is 8½ cwts. to the charge of 35 tons, or 1·2 per cent. only. The "copper" furnace is provided with two water jacketed tapholes on the long side facing the softening or "antimony" furnaces, and as soon as one of these is ready for a new charge the lead is run into it by means of a movable clay-lined iron gutter from the nearest taphole of the drossing furnace, any litharge or skimmings which it is intended to add as oxidising agents for the antimony being charged at once.

The process of softening is conducted as usual, and generally takes about eighteen hours. Usually five skimmings are made, and the total skimmings from a charge of 32 tons drossed (or 35 tons original) lead amount to about 36 cwts. containing on an average 12 per cent. antimony. The consumption of coal averages 28 cwts. per charge, or just 4 per cent. on the original bullion, making a total consumption of 5·2 per cent. by weight for combined drossing and softening. Each furnace is worked by one man per shift. The loss by volatilisation, working at this low temperature, is very slight, and the system of using separate drossing and softening furnaces has much in its favour besides economy of fuel, for the drossing furnace, if carefully handled, lasts indefinitely, and even on the softening furnaces repairs are much lighter, owing to the almost constant temperature at which they are kept. The complete separation of copper in the first furnace, moreover, much simplifies the subsequent treatment of bye-products, particularly of the antimony skimmings. Furthermore, the perfection of the softening, coupled with the low temperature in the desilverisation pots, renders it possible to produce very rich gold and silver crusts, which means less lead to be cupelled and smaller losses of silver.

Refining in Reverberatories.—The same furnace is used as for softening, but it is frequently made 3 inches shallower. The desilverised lead is syphoned into it by means of the Steitz lead syphon made of gas pipe, one form of which is shown in Figs. 120-121, or by means of the Rösing lead pump, if the works are on a level. The mode of operating is similar to that in the softening furnace, except that a higher temperature is necessary, and that zinc, and not antimony, is the principal metal to be oxidised. The last traces of antimony, however, when the lead has not been thoroughly softened, are very difficult to remove in refining, and, therefore, a lead containing 0·6 per cent. of zinc and 0·3 per

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cent. of antimony will yield as much as 4 or 5 per cent. of skimmings containing about 90 per cent. of lead.* These skimmings are removed in separate "heatings," the doors being thrown open for a time to cool the skimmings and render them easier to remove. Three heatings are usually required, taking about twelve hours, after which the litharge drawn from the surface of the bath should be bright yellow and free from brown spots (antimony). Steam is now rarely used in refining furnaces, for the same reasons as are given in connection with softening furnaces.

Refining in Kettles. — Refining at Lautenthal has been already described. Whenever the work in the softening furnace has been very thoroughly done, the lead, after desilverisation, may be economically refined in pots, as it is antimony and not zinc which brings about the greatest destruction of pots.

At the *Port Pirie* refinery, kettle refining is practised. The kettles (here called "pans") are 8 feet 6 inches diameter and 3 feet 4½ inches deep, holding, when full, 30 tons each; they are provided with movable steam pipes reaching to the bottom, and with a hood similar to those at Lautenthal. The life of each pot is about thirty-five charges, or about 850 tons of lead refined, the thickness of cast iron being 1½ inches at the bottom and 1¼ inches at the rim, and the weight, when new, 52 cwts. each. Steel kettles have been tried, but were not a success—possibly on account of poor quality of steel.

The usual charge for one of these kettles is about 24½ tons of desilverised lead from the zincage pots, with 0·67 per cent. Zn, which, by strong firing, is brought to a dull red heat; the hood is then lowered and steam blown through for four hours, at the end of which time the lead has become comparatively cool; the hood is then raised so as to remove the first "refining skimmings," which amount generally to about 2400 lbs. (or, say, 5 per cent. of the weight of lead charged) and contain 75 per cent. lead and 15 per cent. zinc. The lead is then again heated red hot and steam again passed for half an hour. The second skimmings then removed weigh about 350 lbs. and contain only 0·5 per cent. zinc. The lead is then maintained at an even temperature and cast when convenient. As a rule, each charge takes about sixteen hours to work off (including casting) and consumes about 12 cwts. of coal, or 2½ per cent. of the weight of lead charged (according to Hofman,† 6 per cent. is required in American works).

Casting.—The operation of casting (or "moulding" as it is often termed) from refining kettles is a very simple one, the syphon employed being more or less similar to that shown in Figs. 120 and 121, the flow of which can be slackened or stopped entirely by raising the end of the movable arm. In use, this

* Hofman, *op. cit.*, p. 341. † *Op. cit.*, p. 341.

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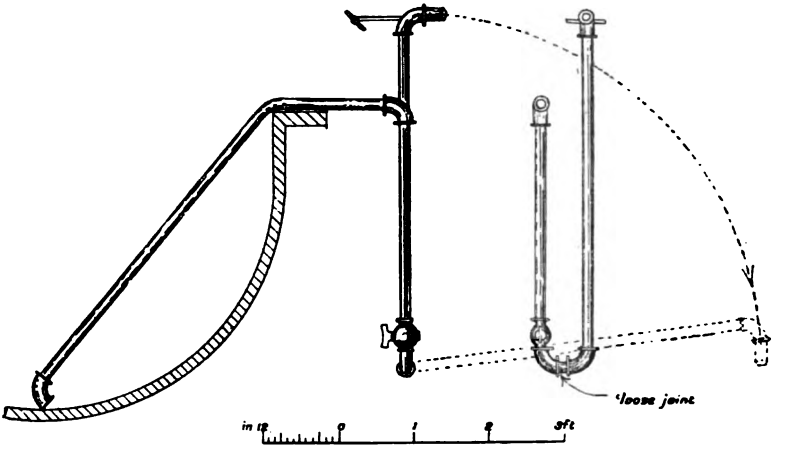
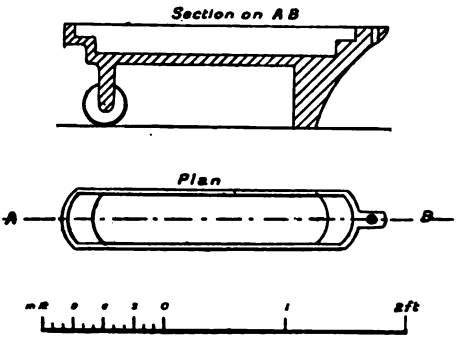
syphon must be firmly clamped to the kettle by means of two hoops which encircle it.



Figs. 120 and 121.—Syphon.

The moulds used are commonly mounted on a wheel like that shown in Figs. 122 and 123; forty to sixty of these, arranged in a semi-circle round the end of the syphon, are used at once.

When the lead has been refined in a reverberatory furnace, it may be cast direct from the furnace. The apparatus used



Figs. 122 and 123.—Mould.

for this purpose is shown in Fig. 124. This method of casting has obvious advantages, but it has the grave disadvantage of requiring the refining furnace to be cooled down for moulding with a loss of, at least, the two hours required to heat it up again,

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besides the increased strain on the furnace and wear and tear of the lining. Hence it is decidedly preferable to tap into a warmed merchant-kettle and cast at leisure when the lead has attained the right temperature, either by means of the Steitz syphon or of the Rösing lead pump.

Some data with reference to softening furnaces at different works are given in Table XXXIV.

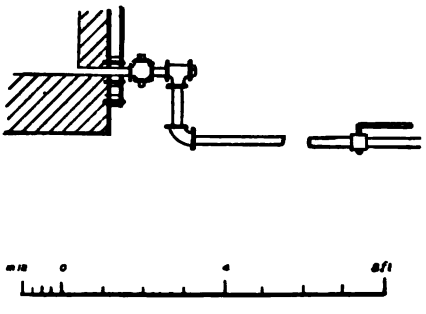

Fig. 124.—Apparatus used in direct casting.

TABLE XXXIV.—Work Done in Softening and Refining Furnaces.

	Freiberg, Saxony.	Omaha and Grant, Omaha, Neb.	Port Pirie, S.A.	Howdon Works, Newcastle-on-Tyne.
References, . . .	1.	2.	3.	4.
Softening—				
Weight of charge in furnace, tons,	21	45	35	140
,, dross removed, ,,	...	...	3	...
,, skimmings produced, cwts.	...	...	36	...
Number of hours in furnace, . .	36	12	27	48
Percentage of softened lead, . .	85	...	86	...
Weight of coal used per charge, tons,	...	1½	1¾	...
Percentage consumption of coal, .	...	3·3	5·2	2½
Men employed per 24 hours, . .	...	3	3	...
Percentage of antimony in skimmings, ...	...	..	6	...
Refining—				
Weight of charge, . . tons,	...	...	24½	...
,, skimmings removed, cwts.	...	...	24	...
Percentage of market lead, . .	...	...	95	...
Time taken in refining, . hours,	9	12-18	16	...
Percentage of Zn before refining, .	0·75	...	0·70	...
,, ,, after ,, .	0·0002	...	0·0001	...
Silver in market lead, . per cent.,	0·0007	...	0·0009	...
,, ,, ,, dwts. per ton,	4½	...	5½	...
Percentage consumption of coal, .	...	6	3½	...

References.—1. Plattner, *Oesterr. Z. f. B. u. H. W.*, 1887, p. 421. 2. *Private communication.* 3. *Private notes*, 1896. 4. *E. and M. J.*, Feb. 23, 1895.

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Bye-products of the Softening Furnace.—The ordinary bye-products of the softening furnace are two—viz., **copper dross** and **antimony skimmings**; sometimes, as at Freiberg, a third intermediate product of "tin skimmings," but usually traces of tin go into the ordinary antimony skimmings.

Copper Dross.—This is usually worked up by liquating at a low temperature in a liquating furnace, which is frequently built like a small softening furnace, but kept only for treating the bye-products. After as much lead has melted out as possible, the dry dross floating on the metallic bath is raked off, and a fresh charge of dross added; the lead is tapped out into a pot from time to time, and goes back to the bullion-softening furnace.

The **liquated dross** varies in composition according to the nature of the bullion from which it has been derived; some analyses of this substance have been given in Table XXXIII. It usually contains about two-thirds the silver contents of the unsoftened bullion, and, perhaps, 80 per cent. of lead, with 10 or 12 per cent. of copper. It is usually smelted in the refinery cupola to copper matte, together with ores or, preferably, as at *Port Pirie*, with low grade ore-matte, which it raises in copper contents, at the same time that a comparatively clean work-lead is produced carrying most of the silver in the charge.

Antimony Skimmings.—These are also first liquated, with the double object of extracting the shots of metallic lead mechanically entangled, and of desilverising the skimmings, which, before liquation, contain 6 to 15 ozs. silver per ton with base bullion of 300 ozs. Frequently the same furnace is employed as that used for liquating dross, the flame being made as smoky as possible in melting down, in order to reduce lead and carry down the silver; a little fine coal is also thrown on the surface of the bath with the same object. The contents of the furnace are tapped into a large overflow pot with a spout, in which the lead collects, while the liquated skimmings overflow into slag pots. An antimonial lead-copper speiss is often found beneath the cones of cooled skimmings, which is worked up by smelting with the dross.

The **liquated skimmings** are smelted with a calcareous slag from a previous campaign in a small water-jacketed cupola, together with sufficient galena to reduce all the antimony and lead in the skimmings to metal without forming matte. The resulting products are **hard lead** or **antimonial metal**, containing from 7 to 25 or more per cent. of antimony, and an antimonial leady slag, which is saved for the next campaign.

The crude hard lead usually contains a good deal of copper, and is best melted down at a low temperature and drossed to get out as much copper as possible; after which it is poled in the tap kettle to remove the remainder, and sold to typefounders or used for making alloys like Babbitt and Britannia metals.

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The composition of some hard leads and hard lead drosses is given in the following Table:—

TABLE XXXV.—ANALYSES OF HARD LEADS AND HARD LEAD DROSSES.

	Freiberg.	Lautenthal.	Przibram.	Broken Hill.	Clausthal Dross.
Reference, . .	1	2	3	4	5
Pb, . .	81·5	82·08	74·886	72·5	22·962
Ag, . .	...	0·003	0·009	0·07	...
Sb, . .	15·0	17·34	24·270	24½ to 26½	38·763
As, . .	2·5	...	0·109	1 to 3	...
Cu, . .	trace	0·62	0·160	trace	37·643
Ni, . .	...	...	0·015	...	...
Fe, . .	...	...	0·018	trace	0·139
Zn, . .	...	...	0·009	...	0·232
Sn, . .	0·3	...	0·524	...	...
S, . .	...	...	...	...	0·240
	99·3	100·043	100·000	...	99·979

References.—1. *J. f. d. B. u. H. W. in Sachsen*, 1883. 2. Schnabel *Handbuch der Metallurgie*, vol. i., p. 434. 3. *Oesterr. Jahrb.*, vol. xxxix., p. 64. 4. *Private notes.* 5. *B. u. H. Z.*, 1870, p. 169.

An American way of treating dross and skimmings from the softening furnace is to smelt both together in a reverberatory furnace with a small quantity of galena ore low in silver. The products are **work-lead**, containing most of the silver contents of both dross and skimmings; high grade **copper-lead matte**, free from iron; and **refined antimony skimmings**, freed from both silver and copper, and, therefore, suitable at once for smelting to antimonial metal. The furnace has two tapholes, from the upper of which the refined skimmings are tapped, the lower one serving for lead and matte. The lead goes to the softening furnace and is treated like the ordinary work-lead.

The **copper-lead matte** is charged into an English cupelling furnace (*v.* Chap. xviii.) and oxidised, with the addition of siliceous sand or broken quartz. The products are lead slag, which runs off continuously into slag pots, and a mixture of 60 per cent. copper matte with some metallic bottoms, which collects on the test. When full, the contents of the test are tapped into moulds; the **copper bottoms**, containing all the gold of the dross and skimmings, are worked up by solution processes;* while the gold-free copper matte, rich in silver, is

* *v.* Part II., Silver, Chap. xviii.

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cupelled up to argentiferous metallic copper in another hearth, and used as a precipitant for the silver in parting doré silver* bullion. In this way all the metallic constituents of these bye-products are utilised in the most advantageous way, except the part volatilised, which is rather more than usual, owing to the high temperature and intense oxidation of the cupelling hearth.

At *Port Pirie* (S.A.) the antimony skimmings are smelted in a small reverberatory furnace built in an iron tank like a softening furnace. Twelve charges are run through in twenty-four hours, each being composed of 1¼ tons skimmings and 115 lbs. of coke breeze; the lead from four successive charges is allowed to accumulate in the furnace, and is only tapped at every eight-hour shift, while the slag accumulates till, at the end of twenty-four hours, the whole charge is tapped out into a tap pot. The product from each ton of skimmings is 1200 lbs. of liquated lead containing 1 to 2 per cent. Sb, 1½ per cent. Cu, and all the silver of the skimmings, generally amounting to about 35 ozs. per ton. The remaining lead contents of the original skimmings (except about 7 or 8 per cent. loss by volatilisation) are contained in the "antimonial slag" (elsewhere called "liquated" or "refined" antimony skimmings) which contains 46 to 53 per cent. lead and 17 to 24 per cent. antimony.

The "antimonial slag" is then smelted with fluxes in a small 5 feet by 3 feet furnace at the rate of 24 tons per day. The charge is ordinarily 450 lbs. of antimonial slag, 350 lbs. returned slag from a previous operation, 50 lbs. limestone, and 100 lbs. ironstone, which is smelted with 75 lbs. coke. The yield is 70 per cent. by weight of the antimonial slag charged as the so-called "antimonial lead" containing 25 to 30 per cent. of antimony. This product is so free from copper and silver that it can be sold at once to the typefounders.

The treatment of tin skimmings at Freiberg (which contain PbO 70·35, SnO_2 12·53, Sb_2O_5 12·50, As_2O_5 4·73, CuO 0·61, and Ag 70 ozs. per ton) consists of a succession of softenings in a reverberatory, and smeltings of the skimmings in a cupola which need not be described here. The final product is a desilverised alloy, containing Sn 33 per cent., Sb 14 per cent., As 1 per cent., which is readily marketable. For details the student may consult the original paper of Plattner. †

Bye-products of the Refining Furnace (or Kettle).—In refining there is only one product, namely, *refining skimmings*, which is, properly speaking, a bye-product of the Parkes process, but may be conveniently referred to here.

These skimmings are mixed with 10 per cent. of fine coal and smelted, preferably in an English reverberatory furnace. The

* *i.e.*, silver containing gold.

† *Berg- u. Hüttenm. Zeitung*, 1883, p. 417; also abstract of same in Schnabel, *op. cit.*, vol. i., p. 431.

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temperature is gradually raised till no more lead runs, when the residues are rabbled, collected, and drawn. The lead goes back to the refining furnace, the residues, which, besides lead, contain much zinc and some antimony, as well as traces of other metals, are treated together with the softening skimmings, or returned to the ore blast furnace together with litharges, &c., as lead flux for siliceous ores.

At *Port Pirie* the first and second refining skimmings are treated separately. The former, containing 75 per cent. Pb, 15 per cent. Zn, and about 0·3 oz. silver per ton, are treated in the refinery blast furnace, together with litharges, mattes, and other products. The latter, containing 96 per cent. Pb, 0·5 per cent. Zn, and ½ oz. Ag per ton, are added to the softening furnace, where they assist in the expulsion of antimony. This would seem to be about the best possible way of handling these skimmings.

CHAPTER XVI.

THE PATTINSON PROCESS.

This process is based upon the discovery of Pattinson in 1829 that the crystals which form during the slow cooling of molten lead are poorer in silver, while the still liquid remainder is richer in silver than the original lead. This is explained by the experiments of Reich,* who found that small quantities of silver alloyed with lead lower its melting point until the silver contents rise to about 700 oz. per ton (2¼ per cent.), above which critical point the higher melting point of silver exerts its influence, and subsequent additions of that metal raise the melting point of the alloy.

In the case of poor leads subjected to cooling from a molten condition, if two-thirds be removed as crystals these will be about one-quarter as rich in silver as the liquid remainder, which is ladled out into another pot and allowed to accumulate till there is enough for a repetition of the process, or lead of equal tenor from some other source is added. By a sufficient number of repetitions the liquid remainder from the last crystallisation is raised to about 500 to 600 ozs., when the process has to stop, the enriched lead being cupelled.

Interference of Impurities.—Most impurities of the work-lead interfere with the process, because they tend to hinder the

* *Berg- u. Hüttenmännische Zeitung*, 1862, p. 251.

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formation of large crystals, besides producing a large quantity of dross.

Arsenic, *antimony*, and *tin* are especially deleterious, the former passing chiefly into the crystals, while the two latter are to some extent concentrated in the liquid lead. *Zinc*, also, if present (which, fortunately, is but rarely the case), is fatal, causing, even in small quantities, a reversal of the process, the silver going into the crystals and dross, as in the Parkes process. *Copper* is largely eliminated as pot dross, but to a slight extent becomes concentrated in the residual lead. *Bismuth* is very perfectly concentrated in the latter (as is also *nickel*); upon this fact is based the Freiberg process for its commercial utilisation. When the lead is free from As, Sb, and Cu, a simple "poling" in the pot in which it is melted down and removal of the dross is sufficient preliminary purification; but when these impurities are present it must be previously softened.

There are two main variations of the process, namely, *Hand and Steam Pattinsonisation*. In the former a series of eight to fifteen cast-iron pots is employed; into one of the central ones the lead is introduced and melted down; it is then cooled, with water and by constant stirring, until crystals form, which are ladled out with a perforated skimmer into the pot on the right, while the liquid lead is ladled into that on the left. In the latter process, only two melting pots and a crystalliser are required, stirring is done with a jet of steam, and, instead of ladling out the crystals, the still liquid lead is drawn off into moulds from the bottom of the crystalliser. This process is an improvement on one now obsolete, in which mechanical stirrers were employed.

HAND PATTINSONISATION.

Plant Employed.—The number of the pots employed varies, according to the richness of the lead, from eight to fifteen, all of which are arranged in a row side by side to form a so-called "battery." Part of such a "battery" of Pattinson pots is shown in Figs. 125 and 126, in which A A are the pots, *b b* the fireplaces, *c* a ring of brickwork which both helps to support the pot and separates the fireplace from the annular flue, *e*, round which the flames circulate before passing by the downtakes into the flues, *d*. It will be seen that each pot is fired independently of its neighbours; all the pots are of the same size, except that on the extreme right, called the "market pot," which, having only to receive the desilverised lead, is usually only two-thirds the size of the remainder. The crystals are removed from the pots, sometimes by perforated hand ladles, but more usually by larger ladles worked by small cranes.

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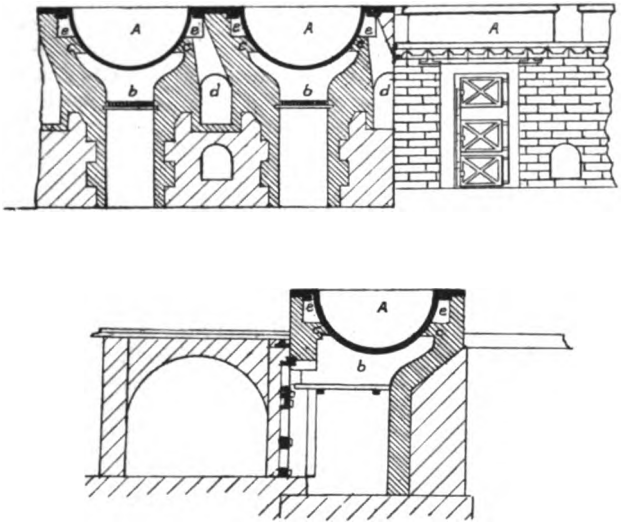
Mode of Working.—Two methods are in use, called the method by **thirds** and that by **eighths**. In the former, two-thirds of the lead is allowed to crystallise and is removed to the right, and the remaining one-third of enriched lead, which is twice as rich as the original lead, or nearly four times as rich as the crystals, is passed to the left. In the method by eighths, seven-eighths of each pot is removed as crystals, and the remaining one-eighth of liquid alloy is three times as rich as the original lead. This system requires only two to six pots, and is suited to the treatment of very low-grade leads, as the



Figs. 125 and 126.—Pattinson Pots.

concentration in any given pot is more rapid; it was formerly in use near Stolberg (Rhen. Pruss.) for the treatment of lead carrying only 16 ozs. silver per ton, the resulting market lead containing 6 dwts. and the enriched lead 400 ozs. per ton. The method by eighths is, however, complicated and involves the accumulation of numerous heaps of crystals in various stages of concentration.

The method by **thirds** is the common mode and requires from ten to twelve, or even fifteen pots, according to the richness of the final lead produced. The bulk of the work-lead to be treated is melted down in the "charging pot," but the position of this charging pot in the series varies with the proportion of silver in the lead in silver. The pots are numbered in order from the market pot upwards, and the charging pot may be, in a series of twelve pots, anywhere between No. 6 and No. 10. At each

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particular works the silver contents of each pot are kept as far as possible constant, and leads of very different grades may be melted down, each in that pot to which its silver contents most nearly approximate. The average silver contents of each pot at several different establishments is given in Table XXXVII.

The pots are kept whitewashed, in order to prevent corrosion by the litharge which forms, as well as to prevent adhesion of the side crusts which collect on cooling. The lead being melted down in the charging pot is "drossed" with a perforated skimmer, sawdust being sometimes added in order to facilitate the drying and collection of pasty skimmings, and, if no previous softening has taken place, a "poling" with green wood is appropriate at this stage. After skimming again, the fire is withdrawn and transferred to some other pot which is in the melting-down stage, and water is sprayed on the bath from a hose. The crusts which form round the sides are broken off with a chisel-bar and pushed down again to be remelted, while the bath is continuously stirred in order that it may cool as uniformly as possible throughout. Crystals now form in the liquid, and are removed either by the long-handled hand-ladle, or by the much larger perforated ladle, which is lowered into the pot sideways, filled and raised. In either case after jerking and draining on the edge of the pot the crystals are transferred to the next pot "down the house"—*i.e.*, to the right—while after two-thirds of the charge has been thus removed, the remaining one-third of still liquid lead is ladled into the adjoining pot "up the house"—to the left. If there is lead on hand equal in silver contents with that in the pots to the right and left respectively, a similar operation can now be commenced with each of these simultaneously.

If only lead of one grade is being treated, two or more charges of original lead are carried through the series of pots "down the house," being crystallised in each pot successively before enough is accumulated for a crystallisation in the pot next above the charging pot. Generally speaking, at the commencement of any given campaign, all the pots on the right of the charging pot are about one-third full of lead, and those to the left are two-thirds full; the two-thirds of crystals which pass to the right, and the one-third of liquid lead which passes to the left, then form charges for crystallisation both right and left all the way down and up the series. With 12-ton pots the additions of original lead will be sometimes 9 tons and sometimes only 36 cwts., according to the state of the charging pot.

It is but rarely that lead of a single grade is treated in any given plant, and leads of higher or lower silver contents are added to that pot the richness of which most nearly corresponds to their own. Control of the working of the plant is kept by a daily or occasional assay of each pot; if it be found that the

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lead in the market-pot is getting somewhat too rich, the contents of each pot from the market- to the charging-pot are ladled back one step into the pot immediately above it.

The rich lead in the last pot on the left is often still further concentrated, after ladling back the usual two-thirds as crystals into the pot below, by allowing it to cool still further, pressing the large perforated ladle into it so as to keep back the crystals, and then dipping out only the liquid portion which runs into the bowl. In this way the so-called "bottoms" may be as much as twice as rich as the crystals which are ladled back into the pot below.

In another modification of the process, five-sevenths are removed as crystals, and two-sevenths left as enriched lead. This is not very different to the ordinary method of thirds; but almost every works has some little peculiarity of manipulation in carrying out the process.

Examples of Hand Pattinsonisation.—The hand process has been, at several localities, replaced by the steam-stirring process, but it still survives in a few localities and notably at several English works,* also at Linares, Freiberg, and one or two other places on the Continent of Europe.

At *Linares*,† lead of 12½ ozs. is concentrated up to 60 ozs. in a battery of nine pots. The average life of these pots is three years, and the loss of lead is about 1½ per cent. Further particulars as to cost, &c., are given in Table XXXVII. at the end of the chapter.

At *Freiberg*, ‡ a special reason is found for retaining the Pattinson process in the bismuth contents of the work-lead, which averages 0·04 to 0·06 per cent. Bismuth, as already observed, becomes concentrated in the liquid lead, so that the original lead, containing from 133 to 257 ozs. of silver per ton, and 0·05 of bismuth, is concentrated in four crystallisations into a rich lead with 650 ozs. silver per ton and 0·17 per cent. bismuth. The impoverishment of the lead, however, is only carried to the point where it assays 33 ozs. silver, the further desilverisation of this poor lead, now containing less than 0·02 per cent. Bi, being carried out by means of the Parkes process. The recovery of the bismuth from the rich lead during the cupellation of the latter is referred to in Chapter xviii. It is found that by the combined process there is a saving of 18 to 20 per cent. on the total cost of desilverisation as formerly carried out by the Pattinson process alone, besides a better recovery of silver, the market lead now containing only 4½ dwts. as against a former minimum of 6 to 8 dwts.

* *E.g.*, Walker, Parkers & Co., Deebank; and Foster, Blackett & Wilson, Newcastle-on-Tyne.

† *Oesterreichische Zeitschrift für Berg- und Hütten-wesen*, 1887, p. 421; also *Berg- u. Hüttenm. Zeitung*, 1887, pp. 45, 192.

‡ *Priv. com.*, H. W. Pearse, Sept., 1896.

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Cost of the Process.—This varies at different localities from about 7s. up to 15s. per ton, according to the poverty or richness of the lead treated and to the cost of labour and materials; some detailed figures are given on Table XXXVII.

Mechanical Pattinsonisation.—This modification—using a mechanical stirrer in a deep cylindrical pot—was introduced in the sixties to do away with the very heavy labour involved in the hand process, which is only economical where the current rate of wages is very low. Its complexity seemed to more than offset the slight economy of labour effected; and though in successful use for some years at Rouen (France) and Stolberg (Germany), the process has been quite obsolete for the past twenty years. A good description is to be found in the work of Schnabel.*

STEAM PATTINSONISATION.

This improvement on the hand process, invented by Luce and Rozan at Marseilles, has largely displaced the older process, and is in use at Newcastle (Cookson's works), Marseilles, Przibram, and other places in Europe, as well as at Eureka (Nev.).

Plant Employed.—The apparatus used at all the above places consists of two melting pans, which are used alternately, and a crystalliser, besides large oval moulds for the liquid lead of each charge, and a steam-crane to handle the ingots of lead. The plant at Przibram is shown at Figs. 127 and 128.† In these *a a* are the two cast-iron melting pans, each of which, holding 7 tons of lead, can be raised by means of the crane, so as to pour its contents through the spout over the inclined plate, *c*, and the trough, *d*, into the cast-iron crystalliser, *e*, which holds 20 tons, and is covered with the wrought-iron hood and pipe, *f*, to carry off the escaping steam and fumes. Each melting pan is heated by a separate fireplace, *g*, the furnace gases passing either round the annular flue, *h*, which serves to heat the upper part of the crystallising pot, and so down the flue, *i*, connected with the chimney; or, when the crystalliser is to be emptied, down the flue *j*, and along a narrow flue which runs under the discharging spouts *k*, in order to keep them hot, to the flue *l*. The furnace gases can also pass direct to the chimney through the flue *m*, their course being regulated by the dampers *n* and *n'*. The crystalliser itself is heated by a separate fireplace, *o*, the products of combustion circulating round the lower annular flue *p*, and thence passing to the flue *l*. The discharge spouts, *k*, have planed outside flanges, and are closed by means of slide valves working on these flanges and moved by hand levers;

* *Op. cit.*, p. 570; see also Phillips, *Elements of Metallurgy*, 1891, p. 691.

† Zdrahal, *Oesterr. Jahrbuch*, vol. xxxiv., p. 1; also Hofman, *Metallurgy of Lead*, 1893, pp. 302 and 303, from which this description is abridged.

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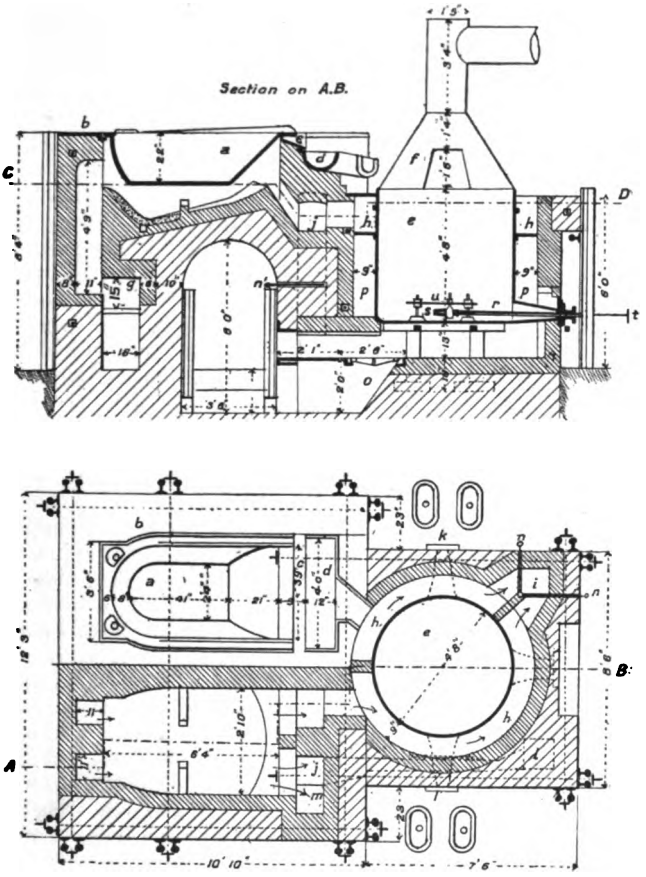
when opened, the molten lead runs through a movable trough into the moulds, *g*, which hold over 3 tons, and into each of which an iron hook is inserted before tapping out the lead to serve as a handle for the block.



Figs. 127 and 128.—Przibram Pattinson Plant.

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The steam inlet* consists of a steampipe, *r*, screwed into a nozzle, *s*, provided with a plug valve, which is opened and closed by means of a rod, *t*, running through the pipe and screwed into the flange. The steam issuing from the nozzle, *s*, is distributed evenly through the lead by means of the perforated baffle plate, *u*.

Mode of Working.—The lead is melted down in one of the melting pans, which takes six hours, drossed, and run into the previously heated crystallising pot by raising the back end of the pan with the crane. Once in the crystalliser, the fire underneath is withdrawn, and the discharge spouts warmed up; steam is turned on for two minutes, and the lead drossed through the doors in the hood. The bath is stirred by means of a jet of dry steam at 45 lbs. pressure, and cooled by spraying a little water from a pipe at the top of the hood, taking care to inject only a little at a time to avoid explosions. After fifteen minutes the steam is shut off, while the crusts which have formed round the sides are barred off through the doors in the hood, and the splashes of lead on the hood are scraped down. This shutting off of steam is repeated about twice, and at the end of about an hour two-thirds of the lead has crystallised. The steam valves are so arranged that this point is indicated simply by the resistance to the passage of the steam being so great as to prevent it from passing up through the lead, so that the cessation of boiling in the lead-bath indicates the completion of the operation.

The steam is then shut off, the slide valves opened, and the still liquid lead run into the moulds with their iron eyes. The fire under the crystalliser is then replaced, and the remaining two-thirds of crystals (say, 13½ tons) is remelted, which takes about three hours; in the meantime 6½ tons more lead, with the same silver contents as that in the crystalliser, have been melted down in one of the melting pans, so that as soon as the crystals are remelted it can be run in and a new operation begun. The other melting pan contains lead equal in value to the crystals which it is expected to produce from the next operation, which is being melted down in readiness for the crystallisation next following. In this way each complete operation on 20 tons of lead takes four hours, all the work being done by two men per shift. The consumption of fuel for the whole operation is at Przibram 35 per cent. by weight of the lead charged.

The products from 100 tons of previously liquated lead are (at Przibram) as follows:—

* For details consult Hofman, *op. cit.*, p. 306.

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TABLE XXXVI.

Products.	Weight from 100 lbs. Work-lead.	Percentage of Total Lead Present.	Percentage of Total Silver Present.
Rich lead, ...	42·99	42·58	97·36
Desilverised lead, . . .	44·76	45·01	0·17
Scrap lead, ...	3·02	3·03	0·61
Dross, ...	9·94	8·04	1·45
Flue-dust, ...	0·46	0·35	0·07
Loss, ...	...	0·99	0·34
Total, . .	101·17	100·00	100·00

At *Eureka* (Nev.) the crystalliser holds 50 tons of lead, and the moulds, into which the liquid lead is poured by a movable spout run on wheels, like that shown in Fig. 122, though enormously larger, holding in fact 3 tons each. At this works the lead is only enriched to about 550 ozs., as the subsequent enrichment is so slow and imperfect that it is not considered worth while bringing it any higher.

In Table XXXVII the value of each separate crystallisation at Przibram and Eureka is given, corresponding with the separate pot-assays of the hand process.

Compared with the hand process, the Luce-Rozan modification has only the disadvantages of a greater capital outlay, and greater cost of repairs and renewals. These are more than offset by the advantages, viz.:—saving of three-fourths of the labour, three-fifths of the fuel, and two-thirds of the dross produced in the old process.

Bye-products.—The bye-products of the Pattinson process, besides scrap lead which is as far as possible returned to that part of the process to which it belongs, are only drosses of various degrees of richness, which are frequently collected by means of sawdust sprinkled on the surface of the pots. They are treated by running down in a reverberatory lead furnace with the addition of fine coal; the dross lead thus produced contains most of the impurities of the original lead, and has to be softened before submitting it to a repetition of the process. The average amount of pot-dross and skimmings produced during the Pattinsonisation of poor lead with only 8 ozs. of silver per ton, may be estimated at 20 per cent. by weight; with richer lead the proportion may reach 25 to 30 per cent. The actual *loss* of lead, however, is always small, varying from, perhaps, ½ per cent. up to 2, or, perhaps, 3 per cent., according to the degree of purity.

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TABLE XXXVII.—Examples of the Pattinson Process.

Reference,	1.	Pontgibaud. 1.	Tarnowitz. 2.	Linares. 3.	St. Louis les Marseille. 4.	Przibram. 5.	Eureka. 6.
Modification of process employed,	Hand.	Hand.	Hand.	Hand.	Steam.	Steam.	Steam.
Silver contents of bulk of lead treated,	21 oz.	96½ oz.	35 oz.	12½ oz.	40 oz.	160 oz.	246 oz.
Capacity of pots, tons,	...	10	15	10	13 – 16	20	50
Assay of market pot No. 1,	9 dwts.	9½ dwts.	6½ dwts.	...	9 dwts.	9½ dwts.	1 oz. 8 dwts.
Assay of contents pot No. 2,	18 dwts.	19 dwts.	...	...	...	19 dwts.	2⅜ oz.
,, ,, No. 3,	2 oz.	2 oz.	...	...	...	2 oz.	5¼ oz.
,, ,, No. 4,	4½ oz.	4 oz.	...	...	...	3½ oz.	10 oz.
,, ,, No. 5,	11¼ oz.	7½ oz.	...	* 12½ oz.	...	7 oz.	20 oz.
,, ,, No. 6,	* 21½ oz.	12⅜ oz.	...	...	...	11½ oz.	33½ oz.
,, ,, No. 7,	41 oz.	22½ oz.	...	...	...	21 oz.	55 oz.
,, ,, No. 8,	79½ oz.	37 oz.	...	...	...	32⅜ oz.	84 oz.
,, ,, No. 9,	129 oz.	59½ oz.	* 35 oz.	60 oz.	...	45⅜ oz.	105 oz.
,, ,, No. 10,	220 oz.	* 96½ oz.	...	...	...	62 oz.	157½ oz.
,, ,, No. 11,	...	167 oz.	...	...	...	103⅜ oz.	*246 oz.
,, ,, No. 12,	...	273 oz.	...	...	...	*160 oz.	...
,, ,, No. 14,	...	...	288 oz.	...	523 oz.	274 oz.	515 oz.
,, liquid "bottoms" of last pot,	358 oz.	514 oz.	...	...	...	...	...
Weight of rich lead from 100 tons work-lead,	...	...	12·62 t.	...	...	42·99 t.	...
,, poor ,, ,,	...	...	84·21 t.	...	45·0	44·76 t.	...
Consumption of coal per cent.,	35	45	45	...	12	35	...
Loss in lead per cent.,	...	...	3·2	1⅛	2·1	1·0	...
Gain or loss of silver per cent.,	...	...	+ 0·02	...	– 1·5	– 0·34	...
Cost per ton s.d., labour,	...	...	6 : 0	1 : 6¼	10 : 11¼	...	...
,, ,, fuel,	...	...	2 : 6⅜	4 : 2⅜	4 : 9⅛	...	...
,, ,, castings, tools, repairs,	...	...	2 : 9	0 : 10¾	4 : 11	...	...
Total,	...	...	11 : 3⅜	6 : 7⅜	20 : 8	...	...

Notes.—The charging pot is marked by an asterisk; all silver contents are given per ton of 2240 lbs.

References.—1. Phillips, *Elements of Metallurgy*, 1891, p. 690. 2. Teichmann, *Preussische Zeitung*, vol. xv., p. 44. 3. *Priv. comm.*, H. W. Pearse, Nov., 1896. 4. Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 527. 5. Zdrahal, *Oesterreichische Jahrbuch*, vol. xxxiv., p. 1. 6. Curtis, *Mon. U.S. Geol. Survey*, vol. vii., 1884, p. 163.

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CHAPTER XVII.

THE PARKES PROCESS.

Influence of Other Metals.—This process, foreshadowed by Karsten, but only made practicable in 1852 by Parkes, is based upon two facts—viz., (*a*) the greater affinity of silver for zinc than for lead; and (*b*) the insolubility of zinc-silver alloys in lead which is already saturated with zinc. The process of desilverisation with zinc consists, in brief, of stirring 1 to 2 per cent. of that metal into a bath of molten work-lead, heated to above the melting point of zinc (415° C.), and allowing it to cool, when a crust, or scum, rises to the surface containing nearly all the silver. A repetition of the process with a smaller quantity of zinc produces a lead which is practically free from silver, containing usually not more than about 4 to 6 dwts. per ton, as against 9 to 15 dwts. by the Pattinson process.

Besides *silver*, zinc has an affinity for various other metals, and in particular for *gold* and *copper*, with both of which it combines before taking up silver. Gold is perfectly extracted by the first addition of zinc, and copper enters the zinc crust almost as readily, though not quite so completely. It is noticeable that a gold-copper crust, containing all but the minutest trace of the gold present, is formed long before the lead begins to take up zinc to any large extent, the gold-zinc and copper-zinc alloys being apparently almost insoluble in zinc-free lead, whereas it is impossible to produce a silver crust without first saturating the lead at the given temperature. Seeing that *copper* alloys so readily with zinc, it is important to purify the bullion as completely as possible by softening and repeated drossing before commencing the desilverisation, as, otherwise, a lot of poor copper crust is formed before any silver at all can be extracted, thus consuming zinc and wasting time.*

Bismuth does not at all interfere with the desilverisation, but *antimony*, in the proportion of 0·1 per cent., and *arsenic* in even smaller proportion, not only retard the rising of the crusts, but actually prevent a clean separation from the underlying lead; so that it becomes impossible to turn out market lead of only 6 dwts. silver from work-lead containing upwards of 0·1 per cent. antimony, or 0·05 per cent. arsenic with only three zincings. Fortunately, arsenic is much more readily oxidised than anti-

* *v.* Experiments by Kirchoff in *Metallurgical Review*, vol. i., p. 224; which are also quoted by Egleston, *Metallurgy of Silver, Gold, and Mercury, in the United States*, vol. i., p. 94.

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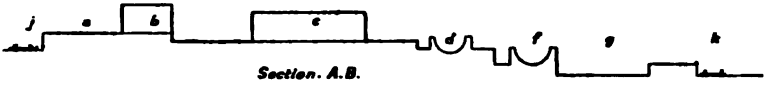
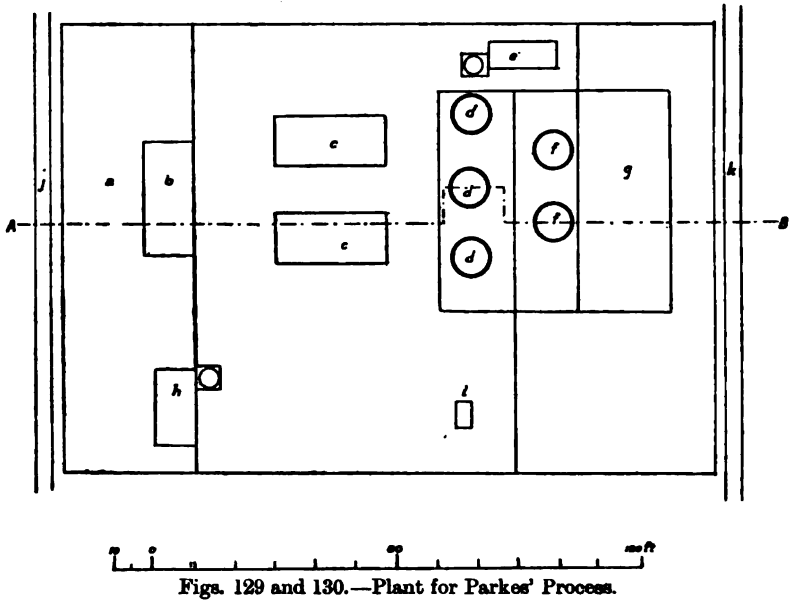
mony, so that it is completely removed after only eight or ten hours' softening, and the question practically resolves itself into the removal of antimony. *Nickel* and *cobalt* (if present) would, like copper, enter the crust, but, fortunately, both metals are easily removed by drossing, besides which they are of rare occurrence.

Impurities in the zinc itself, such as iron, arsenic, copper, sulphur, tin, &c., have the same unfavourable effect as if they were present in the lead; therefore, only the best procurable brands of commercial spelter should be used. This fact was first made clear by the experiments of Kirchoff already referred to.*

Plant Employed.—Lead bullion is always desilverised in cast-iron "pots," "kettles," or "pans," as they are variously called, which are arranged beneath the level of the softening





Figs. 129 and 130.—Plant for Parkes' Process.

furnaces, and above that of the refining furnaces, or kettles, so as to enable the lead to be run from one part of the process to another without undue handling. In some of the older works

* *v.* also Führ, *Berg- u. H. Zeitung*, 1888, p. 28; also Egleston, *op. cit.*, p. 93.

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on the Continent of Europe, Pattinson plants have been made to serve for the Parkes process, with as little alteration as possible, and in these the lead frequently has to be pumped from one part of the plant to another, but in most English and American works the plant is arranged in terrace form, as shown in Fig. 129. This is a sketch section of a somewhat unusual but very effective type of "refinery" (as the whole plant is usually called) arranged like that of the Broken Hill Proprietary Company at Port Pirie, in which the softening is performed in two stages (*v.* Chapter xv.). In this figure and in Fig. 130, which is a sketch plan, *a* represents the receiving or unloading platform, *b* is the so-called "copper," or drossing furnace, *cc* are "antimony" or softening furnaces, *dd* the desilverisation pots, and *e* the liquation furnace for zinc crusts; *ff* are refining kettles, *g* is the casting pot, *h* the dross liquating furnace, and *i* the refinery blast furnace for drosses, skimmings, litharges, &c.; *j* and *k* are sidings for unloading and loading respectively. The retorting and cupellation rooms are situated beyond the crust liquating furnace, in what is practically a separate building.

The pots must be perfectly smooth inside, and are always of cast-iron unless they have to serve for subsequent refining of the lead, when cast-steel is sometimes employed, as already mentioned.* Pots which have to serve for the whole process from drossing to refining, as at *Lautenthal* (Harz) and *Tarnowitz* (Silesia), are made small (12½ to 15 tons); those for desilverisation pure and simple are made to hold from 30 to 50 tons, and may last for 150 to 300 charges. The form is usually a segment of a sphere, and the pot is supported either by a rib cast round it at half its depth, or simply by its flange as shown in Fig. 109. A 30-ton pot is frequently 8 feet 10 inches wide by 3 feet 4 inches deep (the radius being 4 feet 7 inches), and has a flange 9 inches wide. Larger pots are sometimes made elliptical, like those of the Omaha and Grant refining works at *Omaha* (Neb.), which are about 12 feet long by 7 feet wide and 3 feet 3 inches deep, holding 48 tons; but the 50-ton pots of the *Balbach* (N.J.) and *Pittsburg* works are round, like the 40-ton pots of the *Howdon* (Newcastle) and *Pertusola* (Italy) works.

Amount of Zinc Required.—The quantity of zinc required to extract the silver varies according to the richness of the bullion treated, though, proportionately, poor lead takes more than rich. Every refinery has its own table of quantities, and Roswag † has attempted to deduce general formulæ adapted to bullion of any given tenor, which do not, however, seem to have commended themselves to practical refiners. At Freiberg, Plattner ‡ found that the following quantities are required :—

* Chapter xv.

† *La désargentation des minerais de plomb*, Paris, 1884, p. 241.

‡ *Berg- u. Hüttenm. Zeitung*, 1889, p. 117.

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Quantity of Silver in Base Bullion.		Percentage of Zinc Required.
Per cent.	Ozs. per Ton of 2240 Lbs.	
0·0963	31·46	1·34
0·3825	124·92	1·84
0·5080	165·94	1·96
0·8400	256·79	2·45

But much less is found sufficient in most modern refineries by using the crust over again, so as more completely to saturate the zinc contained in it.

Reference has been made to the fact that the gold-copper crust is formed without saturating the lead-bath with zinc. A very small proportion of zinc is, therefore, sufficient for the first or "gold-zinc" addition, as little as 0·10 to 0·12 per cent. by weight being found sufficient for properly softened bullion containing not over 8 dwts. gold per ton,* and subsequent additions are directed solely to the removal of silver. Occasionally, when the bullion contains a large quantity of gold, and is practically free from copper, no separate gold crust is made, but, in that case, all the silver produced from the silver crust has to be parted for gold, and it is far preferable to extract the gold first in as concentrated a form as possible; this is the almost universal modern practice.

When a gold crust is first taken off, the additional zinc, for bullion of 300 ozs. and upwards per ton, is occasionally added in three portions (viz., two-thirds, one-fourth, and one-twelfth respectively of the total); but with ordinary bullion of 150 to 300 ozs. per ton, the work is almost always done with two silver-zincings of about equal amount, say 0·8 to 1·0 per cent. each of the weight of lead under treatment, of which only the second is fresh zinc. Low-grade bullion of less than 125 ozs., if sufficiently softened, can be perfectly desilverised with only two zincings, yielding one gold and one silver crust. The first silver crust from rich bullion should contain from 2000 to 4000 ozs. per ton at least, and leave the lead with 30 to 90 ozs. per ton; the second crust will run from 200 to 700 ozs., and leave a very poor lead; while, if a third addition is required at all, the resulting crust will contain only an ounce or two of silver.

In any case only the first crust is liquated; those obtained from subsequent zincings contain much free zinc and are returned to the pot as the first zincing of the next following charge.

* *Private notes*, Port Pirie, 1896.

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Process of "Zincing."—The pot, having been whitewashed and heated up to the temperature at which a splinter of wood will ignite, is filled with lead by tapping from the softening furnace direct, or by syphoning from a "collecting pot" in which it has been drossed, if such is employed. When it is tapped direct from the furnace a gutter of angle-iron is employed, which empties into an iron pipe reaching to the bottom of the pot, so as to produce as little oxidised dross as possible. In American works the lead is usually drossed at once after addition of any liquated lead from gold crusts of previous charges. Unless, however, the collecting pot has been employed, it is much better to allow the lead to cool in the pot so as to skim off as much copper dross as possible before commencing desilverisation, as this plan permits the complete extraction of gold in an abnormally small weight of gold crust. After drossing, the bath is heated up to about 450° C., and the first addition of zinc is made. The zinc is usually employed in slabs which are simply melted down on top of the lead and stirred in by hand. At some works, however, it is put in a perforated iron box, which is held at the bottom of the pot by an iron rod until the zinc has melted out of it in little streams which can be easily mixed with the lead; at others, again, it is melted separately and poured into the lead, the object in both cases being to avoid oxidation.

However it is melted down, the zinc must be very thoroughly stirred in, which takes thirty to forty minutes; this may be done in two ways:—

Hand Stirring is done by means of a circular perforated sheet-iron disc ("paddle") attached to a 6-foot handle with a crosspiece. Two men on opposite sides of the pot lower their paddles down the sides and raise them in the middle, so producing an upward current in the centre of the lead-bath; the operation is most fatiguing and many attempts have been made to replace it by steam stirring, which, however, has the grave disadvantage of producing a more oxidised and poorer crust; on this account a majority of the best and most modern works still adhere to hand stirring.

Steam Stirring is done by means of a steam pipe reaching down vertically some 2 feet into the centre of the pot. The steam must be perfectly dry in order to avoid explosions, and, therefore, steam traps for condensed water are provided; and the pipe must be thoroughly warmed up before lowering it into the pot. At, or a little above, the melting point of zinc (415° C.) there is comparatively little oxidation of that metal, though at temperatures much above 450° (at a cherry red for instance) oxidation is very rapid. As soon as the steam is turned on it produces a downward current in the centre of the bath, but the bubbles drive away the molten zinc together with the incipient

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crusts to the sides, whence they are continually pushed towards the centre by a wooden hoe.

When the "stirring in" is completed, or somewhat before, the fire is damped down with wet slack and the doors opened so as to cool the pot, and, if steam has been used for stirring, it is blown through the lead a little longer with the same object. After about two or two and a-half hours the surface crust formed begins to adhere to the sides of the pot, and is then removed by means of a perforated skimmer with a long gaspipe handle worked upon the edges of the pot as a fulcrum, or suspended by a hook, which serves the same purpose. At the *Pueblo Smelting and Refining* works (Pueblo, Colo.) the Howard skimmer * is used, which consists of two semi-circular perforated plates hinged in the centre, like a "butterfly valve," and folding downwards. In this condition they are lowered into the lead; they are then unfolded just under the crust, and raised with it above the level of the bath to drain. The crust must be very thoroughly drained and shaken free from lead before turning into the liquating kettle or into a cast-iron mould. That part which adheres to the sides of the pot is then barred off with a long steel chisel, and the operation of skimming repeated till no more crusts form. About eight samples of one A.T. are then taken and cupelled; the silver beads are added together and parted to see if all the gold has been removed.

In the meantime the pot is heated up, liquated lead from the first silver crust of the preceding charge is added, and, as soon as hot enough, the first silver-zinc is stirred in. This consists of the second (and third, if any) silver crust from a previous operation which contains much free zinc, and a little fresh zinc, if necessary, to make up the amount required. The operation of collecting and removing the silver crust is exactly similar to that described for the gold crust; the crust is generally poured and pressed into moulds, so as to be conveniently handled and charged into the liquation furnace.

The lead, now containing from 30 up to 90 ozs. silver, is again sampled and treated with zinc for a second silver crust, which is also generally moulded, or simply deposited on an iron plate close to the pot to wait for the next charge. If, after removing this second silver crust, the lead still contains ½ oz. or so of silver per ton, the necessity for a third zincing can be avoided by blowing steam through the pot for half an hour or more, which causes a small additional formation of zinc crust carrying silver, and reduces the silver contents of the lead to 3 or 4 dwts.

Time Required and Fuel Consumed.—The time required for each melting and stirring averages half an hour to an hour, cooling two to three hours, removal of crusts half an hour to an hour, re-heating one and a-half hours to two hours, so that five

* v. Hofman, *Mineral Industry*, vol. ii., 1893, p. 40.

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to six hours may be reckoned as the average time for each complete zincing. With three zincings giving one gold and two silver crusts, ordinary bullion can be desilverised in about fifteen hours, including running the lead into the pot and syphoning it off afterwards. The *Port Pirie* practice, subsequently described, of doing the work very slowly has many advantages.

The consumption of coal for desilverising and liquating the crusts is about 54 lbs. per ton of original base bullion * (= 2·41 per cent. by weight). At some of the refining works in Chicago, *crude petroleum oil*, sprayed by means of compressed air, is used as fuel, and is said to be more economical than coal, as well as affording the convenience of being extinguished and relighted in a moment, which accelerates both the cooling and the re-heating. Natural gas has also been used at Pittsburg with the same objects and similar results.

Examples of Desilverising Practice.—At *Freiberg*, † lead which has been already partially desilverised by the Pattinson process and still contains 0·1 per cent. Ag (32½ ozs. per ton), is desilverised in 20-ton kettles with three additions of zinc, together amounting to 1·485 per cent. of the weight of lead. The first addition carries off the gold and brings down the silver contents to 8 ozs., while the second reduces it to below 13 dwts., and sometimes to as little as 6 dwts., in which case the third addition is dispensed with.

At the *Port Pirie* refinery, † where 500 tons of lead per week are desilverised, the plant consists of four desilverising pots of 30 tons capacity, and the bullion treated averages 300 to 330 ozs. silver, with about 5 dwts. of gold per ton. Only three zincings are given, and the last of these leaves the lead with only about 6 dwts. silver per ton. The lead is tapped direct from the softening furnace into the zincing pot, where it is allowed to cool for three hours in order to admit of a further drossing which much facilitates the clean separation of the crusts, especially of the gold crust. The amount of "pot dross" removed averages about 200 lbs., containing 210 ozs. Ag, 96 per cent. Pb, and 0·2 per cent. Cu, which is treated together with that produced in the first drossing furnace.

The temperature is then raised, and the *gold-zinc* stirred in. In the first instance, on starting a new campaign a single addition of 75 lbs. zinc is used and is found to extract all the gold. The crust obtained from this very thoroughly softened bullion is found to be still capable of withdrawing most of the gold from a second charge of lead, although the total amount of zinc added is not more than one-tenth the amount required to saturate the lead. It is, therefore, returned to the next potful of lead ready for treatment, from which nearly the whole of the gold is extracted, and the enriched (because twice used) gold crust is

* Hofman, *Metallurgy of Lead*, p. 337. † *Private notes*, 1896.

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set aside until sufficient accumulates for a charge in the liquation furnace. This second pot, however, still retains a trace of gold, so that a second addition of 50 lbs. of fresh zinc has to be stirred in to clean it. The resulting skimmings, which contain most of the added zinc still free, serve as first addition to the next following charge, so that each charge is treated twice for gold, viz., first with once used zinc skimmings, and then with 50 lbs. of fresh zinc. In this way only 50 lbs. of fresh zinc are required for each charge of lead, and a rich gold crust is obtained from poor lead at the expense of only a slight delay.

The perfection of the extraction of gold with this exceedingly small quantity of zinc (only 0·07 per cent.) is remarkable, the lead retaining only about 4 grains per ton, or, say, 1 oz. per ton of silver contained in it, and the Port Pirie practice would seem to be a great improvement on the American practice described by Hofman,* in which 250 to 300 lbs. of zinc are required to obtain a gold crust from bullion of the same richness in gold. It depends entirely, however, upon a much more thorough drossing and softening than is usual in America, and the only possible objection, the greater time it requires, is obviated by the simple expedient of distributing an amount of work usually performed in two desilverising pots over a plant of three, or the work of three over four pots, without any increase in the labour, or in wear and tear of pots, and with practically no increase in the consumption of fuel.

After removal of the second or intermediate gold crust, the lead is again heated up, and the first silver-zinc stirred in; this consists of some 3 or 4 tons of lead-zinc-silver alloy with about 10 per cent. Zn, and about 700 ozs. Ag per ton, obtained as the second silver crust from the previous charge cast into moulds, and stacked by the side of the pots. This is stirred in very thoroughly by hand, and the pot is allowed to cool, the crusts which then rise being skimmed off by hand, drained over the pot, and cast in moulds. The whole process of heating, stirring in, cooling, and removing the principal silver crust takes about eight hours, the full plant of four pots being worked in a leisurely manner, cooling very thoroughly, by a gang of five or six men; this plan has been found to give the best results without consuming any more fuel.

When no more crust rises, the lead (now carrying 90 ozs. per ton) is reheated, and the second silver-zinc, consisting of 825 lbs. of fresh zinc, stirred in. After cooling and skimming the second crust, which is moulded and stacked for the next charge, the lead rarely contains above 6 dwts. Ag per ton. It is at once syphoned off by the ordinary Steitz syphon into the refining pots below. Occasionally, when the lead has been less thoroughly softened than usual, it still retains, after the second zincing, from

* *Op. cit.*, p. 328.

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½ oz. to 1 oz. silver, and in such cases a third zincing is given, using a small quantity only of fresh zinc, which is stirred in and removed at the lowest possible temperature, so as to clean the lead as thoroughly as may be.

The crusts average, after liquation, gold crust, 750 ozs. Ag, 13 ozs. Au, 4 per cent. Zn; silver crust, 4300 ozs. Ag, 17 per cent. Zn. The pots used at the works (and cast locally) last, on an average, during the treatment of about 150 charges. The consumption of fuel is about 18½ cwts. of coal per charge treated, or, say, about 2·65 per cent. of the weight of the original base bullion. The total amount of zinc used is 1·34 per cent.

Some data of desilverising practice at various localities are given in the following table:—

TABLE XXXVIII.—Comparative Data from Desilverising Plants.

	Lautenthal, Upper Harz.	Tarnowitz, Upper Silesia.	Freiberg, Saxony.	Port Pirie, S.A.
Reference, ...	1.	2.	3.	4.
Capacity of desilverising pots, . . tons,	12½	13½	20	30
Silver contents of lead, ozs per long ton,	49	16	33	330
Weight of first zincing, . . . lbs.	49	...	220	75
,, second ,, ... ,,	110	...	165	} 825
,, third ,, ... ,,	180	...	88	
Total weight of zinc employed, . per cent.,	1·21	1·00	1·00	1·34
Value of gold crust, Au, . ozs. per ton,	...	...	5	13
,, ,, Ag, . ,,	...	...	1486	1000
Value of first silver crust, Ag, ,,	...	...	...	3750
,, second ,, ,,	...	...	...	700
Silver contents, lead after first zincing, ozs.,	48	...	8	305
,, ,, second ,, ,,	6	...	13 dwts.	90
,, ,, third ,, dwts.,	3	2	4	6
Total time in desilverisation pans, hours,	15½	22	20	22-24
Coal consumption, . . . per cent.,	9·76	7·4	...	3
Gold contents, original lead, . dwts.,	...	...	2½	6
Percentage of gold crust produced, . .	...	...	...	0·091
,, silver crust produced, . .	6	...	2·25	...
Life of pot, charges, ...	...	...	...	150

References.—1 and 2. Schnabel, *Handbuch der Metallurgie*, vol. i., pp. 540 and 541. 3. Plattner, *Oesterr. Zeitung f. Berg- und Hüttenwesen*, 1887, p. 421. 4. *Private notes*, 1896.

Composition of Zinc Crusts.—Before liquation, it is difficult to determine the average composition of these, owing to the lead which they retain mechanically; even after liquation some free lead still remains, being prevented from running together by

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films of zinc, lead, and other oxides between the globules. Besides gold, silver, copper, iron, &c., *tellurium*, if present, becomes concentrated in the silver crust,* finding its way into the retort bullion, and, finally, into the last litharges, where no doubt it exists as a tellurate of lead.

The following table shows some analyses of zinc crusts :—

TABLE XXXIX.—Composition of Zinc Crusts.

	Liquated Silver Crusts.				Port Pirie, 1897.	
	Altenau, 1880.	Lautenthal, 1880.	Mechernich, 1884.	Freiberg.	Gold Alloy, after Liquation.	Silver Alloy, after Liquation.
Reference, .	1.	2.	3.	4.	5.	6.
Pb, . . .	75·675	77·820	45-48	53·20	85·0	68
Zn, . . .	11·78	12·11	35-45	39·70	4·0	17
Cu, . . .	1·12	0·82	2-3	2·68	5·5	...
Ag, . . .	1·855	2·42	1·5-1·7	4·55	...	...
As, . . .	tr.	tr.	...	...	...	...
Sb, . . .	...	...	0·36	...	...	...
Cd, . . .	tr.	tr.	...	...	...	...
Ni, . . .	tr.	tr.	...	...	...	...
Fe, . . .	...	...	1·28	...	...	...
PbO, . .	4·75	4·00	...	...	...	...
ZnO, . .	0·60	0·44	...	...	...	...
Bi_2O_3, . .	·72	0·37	...	...	...	...
Sb_2O_3, . .	0·63	0·98	...	...	...	...
Fe_2O_3, . .	1·87	1·04	...	...	...	...
Ag, ozs. per ton,	...	...	...	...	750	4300

References.—1 and 2. *Zeitsch. f. d. B. H. u. S. W. i. P.*, vol. xxxviii, p. 262. 3 and 4. *Ibid.*, vol. xxxiv., p. 92. 5 and 6. *Private notes.*

Use of Aluminium-Zinc.†—Not only is the lead contained in the zinc crust prevented from liquating out perfectly by the films of zinc and lead oxides, but the perfect collection of the zinc-silver alloy is also impeded by these same films, and this is the principal reason why it is not possible to desilverise with a single addition of zinc. At temperatures up to 500° the lead will not dissolve sufficient zinc to carry up all the silver present, and if it be attempted to raise the temperature to 700° with the idea of dissolving the whole quantity of zinc at one operation, so much

* Heberlein, *Berg- u. H. Zeitung*, 1895, p. 41.
† *E. and M. J.*, April 4, May 16, 1891, also Sept. 2 and Dec. 12, 1893.

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oxide, both of lead and zinc, is formed that liquation is impossible and a great deal of the silver remains in solution, instead of going into the crust. Any addition, therefore, which tends to prevent oxidation of the lead-bath during the progress of desilverisation will facilitate the operation and yield a richer crust. Such a substance was found by Rössler and Edelmann * in aluminium, one-half per cent. of which completely prevents oxidation of zinc at the ordinary desilverising temperature, while even the amount of 0·007 per cent. Al by weight in the lead-bath which is being desilverised—if free from copper and arsenic, and very low in antimony—practically protects it from oxidation, the surface remaining bright and metallic.

Antimony, in the proportion of 0·1 per cent. or less, does not interfere; 1 per cent., however, interferes very much with the separation, besides causing a high zinc consumption. In the presence of so little as 0·1 per cent. of *copper*, however, or 0·05 per cent. of *arsenic*, the protective influence of aluminium disappears, and oxidation takes place, with consequent incomplete separation of the crust from the lead. All lead bullion, therefore, which is not *very* thoroughly softened requires to be further purified by means of a copper-zincing before adding the aluminium-zinc alloy.

In practice, the Al-Zn alloy, with ½ per cent. Al, is produced by melting the zinc and stirring in the aluminium; this molten alloy, in quantity sufficient to extract all the silver present, is poured into the lead-bath, previously freed from copper and arsenic and thoroughly stirred at a temperature somewhat over 500° C. As the bath cools, two successive crusts are removed, the first (called the "cream crust") containing most of the oxidised material, and resembling ordinary crusts in appearance; while the second, though richer in metallic lead, is almost free from oxides, and carries most of the silver.

At *Hoboken*, near Antwerp,† where this process is carried out on base bullion varying in richness between 50 and 300 ozs., the "cream" or first portion of the crust is from 1 to 5 per cent. of the weight of lead treated, the second portion being from 5 to 9 per cent. by weight, according to the silver contents of the bullion. Both crusts are liquated separately, and, after giving up about 76 to 80 per cent. of their weight as liquated lead, the residues are melted down together, yielding a rich *zinc-silver alloy* and an *oxidised crust*. The former only is perfectly melted; it has a silver-grey colour, a fine-grained fracture, and is free from the iridescent oxidation colours seen in ordinary zinc crusts. It contains 20 to 35 per cent. Ag, 3½ to 5 per cent. Pb, 1½ to 4½ per cent. Cu, and 60 to 70 per cent. Zn, besides traces of Al, Sb, As, and Fe; the oxidised crust contains 2 to 6 per cent. Ag only.

* *Ibid.*

† Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., p. 576; also *E. and M. J.*, Sept. 2 and Dec. 12, 1893.

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The higher percentages of silver above given are only found when treating rich bullion.

When treating low grade *Mazarron* bullion, averaging 49 ozs. silver per ton, which is first softened by steam in the same pot in which desilverisation takes place, the total consumption of zinc is 1·42 per cent. Of this amount, 20 per cent. (0·29 per cent. on the lead) is added at first, and a gold and copper crust removed; then the remainder (1·13 per cent. on the lead), previously alloyed by melting with 0·5 per cent. Al, is poured in after heating the bath. On this poor lead the "cream" crust amounts to 1½ per cent. only by weight, and yields on liquation 62 per cent. of lead, 4 per cent. of rich alloy, and 34 per cent. of oxidised crust; the second, or "rich," crust yields 87·7 per cent. of lead, 9·8 per cent. of rich alloy, and only 2·5 per cent. of oxidised crust.

The weight of each kind of product obtained from 100 parts of unsoftened or original base bullion, and the percentage proportions of silver and lead contained in each are given in the following table :—*

TABLE XL.—PRODUCTS OF DESILVERISATION WITH ALUMINIUM-ZINC.

Products.	Weight of each Product.	Proportion of Values.	
		Lead.	Silver.
Refined Lead,	90·7	90·7	trace
Softening dross,	1·4	1·0†	1·3
Skimmings and pot dross,	4·6	4·0†	trace
Copper crust,	2·9	2·1†	9·9
Rich silver-zinc alloy,	0·6	0·02	78·9
Oxidised crust,	0·7	0·50	9·9
Loss,	...	1·68†	none
	100·9	100·00	100·0

According to Roswag, the average loss in the ordinary desilverisation process without aluminium is 1·60 per cent. of the lead, and 0·3 per cent. of the *true* silver contents of the lead; most refineries, of course, show an overplus of silver caused by loss in the ordinary commercial assay of the base bullion.

TREATMENT OF ZINC CRUSTS AND ALLOYS.

All crusts are separated as far as possible from adhering lead by liquation before being further treated; this may be done either in kettles or in furnaces.

* Adapted from Schnabel, *op. cit.*, p. 577. † Approximations only.

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Liquation in Kettles or Pots.—In this system each desilverising pot has by its side two smaller pots.* The American liquation kettle is always made with a convex bottom, as shown in Fig. 131*a*, but on the Continent the form shown in Fig. 131*b*, is often used.† The liquation pot, of whatever form, must be heated very gradually, otherwise some of the zinc crust will be re-dissolved in the liquated lead. When no more lead exudes, that which is liquated is tapped into the liquated lead pot set below, and the crust is withdrawn and broken up, while still hot and brittle, into small pieces for subsequent treatment. This is done by bruising and cutting it with a shovel, or by forcing it in a pasty condition through an iron grating.

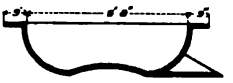

Fig. 131*a*.

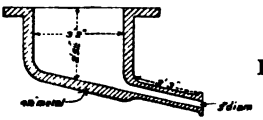

Fig. 131*b*.

Figs. 131*a* and 131*b*.—Liquation Kettle.

The liquated lead amounts to from 40 to 60 per cent. by weight of the crust charged; that from the gold crust assays 100 to 250 ozs. silver per ton, and is added to the desilverising pot before the gold-zinc of the next charge; that from the silver crust assays 30 to 40 ozs., and is added to the next charge before the first silver-zinc. At *Freiberg* the liquated lead from a crust containing 1200 ozs. silver, which leaves the pot lead with 8 ozs. Ag., runs itself only 11 ozs. It may be stated, as a general rule, that when liquation is performed carefully, whether in pots or in furnaces, the liquated lead will run from 30 to 40 per cent. higher in silver than that left in the pot from which the crust was removed.

Liquation in Furnaces.—The liquation kettles are convenient for small works, but at large establishments they are advantageously replaced by furnaces, which treat all the crusts from several desilverisation pots. This simplifies the work at the latter, besides giving more uniform results. The reverberatory has the further advantage that a reducing flame can be employed, so avoiding the partial oxidation which takes place in the pots, and, when not over-driven, it extracts from the crust a larger proportion of poor lead, so yielding a richer liquated crust.

The liquating furnace at *Port Pirie* (S.A.) is shown in Figs. 132 to 134, in which *a* is the fireplace, *b* the bridge, with an air-cooled casting in the centre, and H the trough-shaped hearth, composed of a single course of firebrick inclined towards the centre and lengthwise towards the lead kettle *c*. The whole hearth is built in a wrought-iron pan, which rests upon a course

* From Hofman, *op. cit.*, p. 330. † Schnabel, *op. cit.*, vol. i., p. 544.

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of old rails supported by brick pillars, so as to be air cooled, and there are two working doors, *d*, besides the taphole opening, *e*. The same down-cast flue, *f*, serves for both the furnace itself and for the auxiliary fire beneath the kettle, in which the liquated lead is kept hot so as to be ladled when convenient.

Fig. 132.

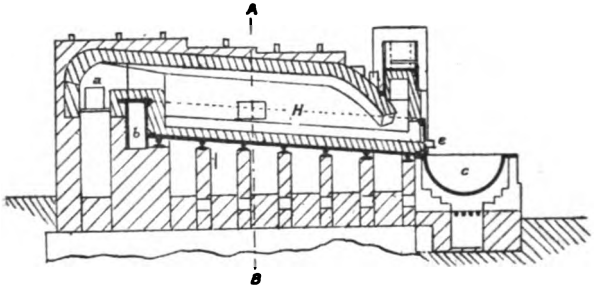
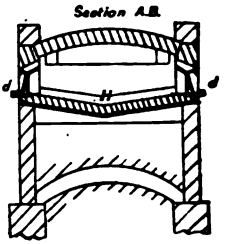


Fig. 134.



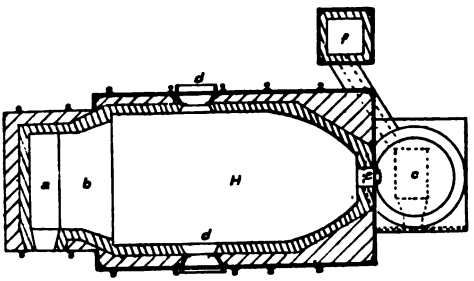


Fig. 133.

Figs. 132 to 134.—Port Pirie Liquation Furnace.

The charge of this furnace is about 1½ tons of zinc crust, which, with the help of constant rabbling and a smoky flame of uniform temperature, is liquated in four hours, the lead accumulating in the lower part of the hearth, from which it is tapped out about twice a shift into the kettle. At first the charge is deposited chiefly at the lower or cooler end of the hearth, and is only drawn upwards nearer the fire as it loses lead and becomes more infusible. The daily capacity of the furnace is about 9 tons of crust, the output of liquated lead is about one-third of the weight of crust charged, and its silver contents average, as already stated, about 40 per cent. more than that of the lead left in the pot from which the crust was removed; thus, at *Port Pirie*, the liquated lead from the silver crust averages about 120 to 130 ozs.,

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while that from the gold crust averages only about 210 ozs. per ton.

The liquation furnaces in American works are generally similar to that just described. The coal consumption in liquation is not generally accounted for separately; it will not average ½ per cent. on the weight of bullion treated.

Treatment of Liquated Zinc Crusts.

The original method of Parkes (1852-59) was to distil off the zinc in an ordinary Belgian furnace, but the retorts would not stand, and the process had to be abandoned for a time. Of late years, however, chiefly owing to the introduction of plumbago retorts and of improved furnaces, this process has again come into vogue and has, to a great extent, displaced other methods, except in a few localities. Three principal processes may be distinguished, the object in each being to separate the zinc and leave the silver in a rich lead suitable for cupellation.

1. **Flach's** process of smelting the liquated crusts with ferruginous slags in a cupola and driving off the zinc into the slag and flue-dust.

2. **Corduries'** process of oxidising the zinc, together with part of the lead, by means of steam at a red heat. Zinc may be recovered as basic carbonate by means of **Schnabel's** process.

3. **Parkes'** process of distilling off the crusts and recovering most of the zinc as metal.

Besides the above processes for the treatment of ordinary zinc crusts with from 4 to 13 per cent. of silver, two special processes, applicable only to the treatment of the rich zinc-silver alloy of the Rössler aluminium-zinc process, must also be briefly referred to, viz. :—

4. The **sulphuric acid** process; and

5. The **electrolytic** process, in which the zinc is recovered as very pure metal.

1. **Flach's Process.**—This process was in use many years ago at several works in England and on the Continent, including the *Mechernich* works. It consisted in smelting down the crusts (in a low square furnace or cupola of 4 to 8 square feet sectional area and not over 8 or 9 feet high, provided with exterior crucible) together with tap or puddle cinder as iron flux to help to carry off the zinc, and sometimes lead matte.* The blast required is of considerable volume, but low pressure (under ½ inch mercury). Any copper in the crust is taken up by the matte, while the silver goes into the lead. None of the zinc, however, is recovered, and the losses of lead and silver in flue-dust and foul pasty slags are considerable; the process has, therefore, been almost superseded by the distillation process hereafter described,

* Hofman, *op. cit.*, p. 348.

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as regards the treatment of silver crusts. At a few places, however, it is still used for the treatment of gold-copper crusts poor in silver, for the bullion obtained by distilling them is very coppery; whereas by smelting them with matte a comparatively soft and easily cupelled bullion is obtained.

2. **Corduries' Process.**—This process, first used at Havre in 1866, is still to be found in a few English and Continental works, notably, in the former, *Walker Parkers'* Flintshire works, and, in Germany, at *Altenau* and *Lautenthal* (Harz).

TABLE XLI.—Products from Corduries' Process.

	Rich Lead.		Rich Oxides.		Flue-Dust.
	Altenau.	Lautenthal.	Altenau.	Lautenthal.	Lautenthal.
Pb, . . .	96·3448	95·1404	37·845	30·065	0·71
PbO, . .	...	...	32·14	36·87	28·20
Zn, . . .	0·0027	0·0023	1·35	1·90	0·12
ZnO, . .	...	...	23·37	23·24	69·60
Cu, . . .	0·8279	0·4645	1·12	1·24	0·17
Ag, . . .	2·4100	3·6500	1·245	1·855	0·03
Bi, . . .	0·0142	0·0169	...	...	...
Bi_2O_3, . .	...	...	0·43	0·44	...
Sb, . . .	0·3914	0·7201	...	...	0·17
Sb_2O_3, . .	...	...	1·06	0·57	...
As_2O_3, . .	...	...	tr.	...	tr.
Fe, . . .	0·0054	0·0044	...	...	...
Fe_2O_3, . .	...	...	1·44	3·82	0·34
Al_2O_3, . .	...	...	...	...	0·24
Cd, . . .	tr.	tr.	tr.	tr.	...
Ni, . . .	0·0036	0·0014	tr.	tr.	...
Insoluble, .	...	...	...	...	0·42
	100·0000	100·0000	100·000	100·000	100·00

The same apparatus is employed as for softening and refining the base bullion.* The charge of zinc crust is 10 tons, which, owing to its semi-oxidised condition, takes eight hours to melt down. As soon as it reaches a cherry-red heat, dry steam, at 30 to 40 lbs. pressure, is turned on and blown through for about four hours. Large quantities of zinc and lead fume (containing some silver) are given off and drawn by means of a steam jet through a suitable series of condensing pipes, which must be water sealed in order to avoid explosions, as the steam becomes partially dissociated, and the escaping gases contain some oxygen as well as large quantities of hydrogen. The pots are rapidly eaten away, only lasting, as a rule, for twelve charges. The consump-

* *v.* Figs. 109 and 110 and accompanying description in Chapter xv.

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tion of fuel is 13 per cent.—viz., 9 per cent. for heating the pots, and 4 per cent. for production of steam. The products are about equal parts by weight of **rich lead** and of **rich oxide**, which floats on the top and is skimmed off, besides **flue-dust**, the amount of which is not stated. Their composition is given in the above Table XLI.*

The **rich lead** is cupelled direct, the **flue-dust** is leached with dilute sulphuric acid to dissolve out the zinc, leaving the silver in an insoluble plumbiferous residue for further treatment. The **oxidised portion** was formerly added, a portion at a time, to the rich lead during cupellation, by which means the greater part of its silver contents became concentrated in the lead, while the oxides removed from the furnace were subsequently smelted with lead ores to recover the remainder. By this process, however, not only was the zinc all lost, but the volatilisation loss of silver was very high. Nowadays, at Lauterthal, the zinc oxide is first removed by Schnabel's process, when the residue is very perfectly absorbed by the lead-bath in cupellation.

2*a*. **Schnabel's process**,† in brief, consists in dissolving out the zinc (and copper) oxide by means of a cold 9 per cent. solution of *ammonium carbonate*, in revolving cylinders holding 1 to 1½ tons, the operation taking twelve hours. The mass is passed through a filter press, which retains the lead and other oxides and the silver; the solution, containing only zinc and copper in solution, passes to a second revolving cylinder, in which it is treated with metallic zinc to precipitate the copper; and then to iron stills, in which it is boiled with steam. The zinc is precipitated as basic carbonate, while the ammonia and one-half the carbonic acid are expelled and condensed in a series of iron Woulff's bottles, through which carbonic acid gas from burning fuel is also passed to make up for that removed by the precipitate. The basic carbonate is converted in small reverberatory furnaces into white zinc oxide, which, however, is inferior in covering power to that produced by sublimation. The consumption of coal is 1 to 1¼ tons per ton of oxides treated.

The advantage of the process consists rather in the decreased loss of silver ‡ than in the value of the zinc oxide produced, which is not sufficient to cover the cost of treatment. The process is now also in use at *Hoboken* (Antwerp), for treating the oxidised portion of the rich aluminium-zinc crusts after liquation. The residues are scorified on a lead-bath and the

* The composition of the original crusts is given in Table XXXIX.; the present analyses are from Schnabel, *op. cit.*, vol. i., p. 562.

† Preuss. Minist., *Zeitschrift für Berg- Hütten- und Salinen- Wesen*, Bd. xxviii., 1880; also Schnabel, *op. cit.*, pp. 564-571.

‡ The silver extracted is usually 1¼ to 2 per cent. above the contents of the oxides as shown by ordinary assay.

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resulting slag does not contain over 0·06 per cent. silver (say 20 ozs. per ton), whereas the slags produced by scorifying the oxides in their original condition without previously extracting the zinc, contained at least 0·3 per cent. silver (say 100 ozs. per ton).

3. **Parkes' Distillation Process.**—This process, since the introduction of plumbago retorts by Morgan in England, and, subsequently, by Balbach in America, has become well-nigh universal for treating zinc crusts. It offers the following advantages:—(1) Quick yield of practically all the silver in the form of rich lead; (2) simple and inexpensive plant; and (3) recovery, in a metallic condition for re-use, of 60 per cent. of the zinc originally used in desilverisation.

Furnaces Employed.—At most refineries in England and on the Continent fixed furnaces are preferred, but in America, where saving of labour is the great desideratum, the tilting furnace of Faber du Faur, used at *Mechernich* and at one or two other places in Europe, is almost universal.

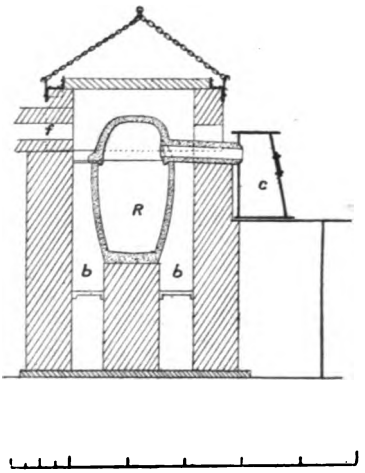

Fig. 135.—Morgan Furnace.

Of fixed furnaces, three principal forms may be mentioned, the first of which is adapted either to direct or to gas heating, the other two being invariably heated by flame from a separate fireplace. In all the illustrations the same lettering is employed to facilitate reference.

a. The *Morgan* furnace is, perhaps, the most commonly employed at English refineries as well as at Freiberg. Its construction is plainly shown in Fig. 135. The plumbago crucible R, 22 inches high, 15 inches diameter, and 2 inches thick, holding 5½ gallons, is provided with a hood and pipe (3 inches diameter) of the same material, to the latter of which is adapted a sheet-iron condenser, *c*. The fireplace, *b*, is packed with coke all round the crucible, which rests on a firebrick pillar, and the top of the furnace is removed by a chain and tackle, as required, while the products of combustion escape by the flue *f*. The charge is about 5 cwts. of crust, taking eight hours to work off, and the crucible lasts for forty to eighty charges. The zinc is removed from the condenser in the form

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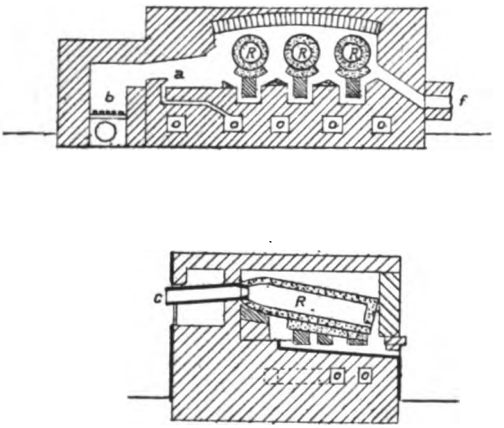
of a lump. The rich lead is dipped out by means of a small pot-shaped dipper attached to a long handle. Other particulars are given in Table XLII.

b. The Continental *tube-retort* furnace, shown in Figs. 136 and 137,* in which R R are the retorts, *c* a condenser, *b* the gas producer, and *oo* channels underneath the hearth of the furnace, through which heated air is admitted to the heating or combustion chamber. Furnaces of this description are in use at *Ems*, *Braubach*, *Tarnowitz*, and other places in Germany, also at *Hoboken* (Belgium). The retorts may be of plumbago, or, more



Figs. 136 and 137.—Tube Retorts.

simply, of mixtures of clay and coke, which, with care in use, last almost equally well. As many as five retorts are placed side by side across the hearth of a reverberatory. Retorts have been made 2 feet in diameter to hold as much as 1 ton each, but the best results are given by small retorts holding about 5 cwts. each. The condensers are of fireclay and plumbago, and the rich lead, after the retorting is completed, is tapped from the bottom of the inclined retort into small moulds. The distillation lasts twelve hours, and each retort lasts from 60 to 130 charges. Other particulars are given in Table XLII.

c. The *flame-heated bottle-retort* furnace in use at *Port Pirie* (S.A.) is shown in Fig. 138. The retort is seen at R, the fireplace (burning coal) at *b*, and at *f* are the exits to the downcast, which connects with an underground flue common to the whole block of twelve furnaces, which are built side by side.

* Schnabel, *op. cit.*, p. 555.

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In all these fixed furnaces the rich lead has to be dipped out by means of long wrought-iron dippers made of a piece of 4-inch pipe on a long handle, or else tapped out from the bottom of the retort; in the tilting furnace the finished charge is poured out direct into moulds.

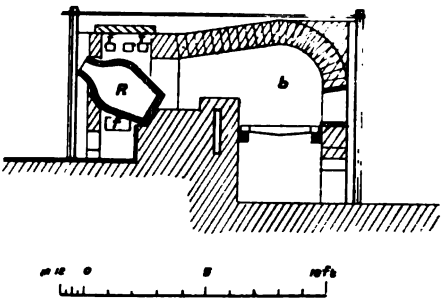

Fig. 138.—Bottle Retort.

d. The *Faber du Faur tilting* furnace, used throughout the United States, and at a few European localities, is shown in Figs. 139 to 142.* It consists of a cubical box of firebrick set in a cast-iron frame swung on trunnions and adjustable by means of a hand wheel working a worm gearing. It has an opening in front for the neck of the retort, one at the back for the products of combustion, and another at the top for charging coke. The retorts are of plumbago and hold from 800 to 1000 lbs., the usual size being 36 inches to 38 inches long, 8 inches wide at the neck, 18 inches to 22 inches at the belly, and 13 inches to 16 inches at the bottom; the thickness varies from $1\frac{1}{8}$ inches at the sides to 2 inches at the bottom. Condensers adapted to the furnace are of various forms and materials, such as cast iron, plumbago, and sheet iron lined with brick or clay; they may rest upon a tripod, hang from hooks on the furnace frame, or rest upon wheels so as to be more easily handled. They may be closed entirely, or, as is more usual, have an aperture for escape of the CO and other uncondensable fumes, and the condensed zinc is usually tapped at intervals into small moulds.

Mode of Working.—Whatever the type of furnace the operation of distilling is substantially the same. The zinc crust, broken to pieces the size of a nut, or smaller, is mixed with 1 or 2 per cent. of powdered charcoal, and charged into the already heated retort by means of a scoop. The temperature is then raised to a bright yellow heat, and more of the crust added as the

* Egleston, *Metallurgy of Silver, Gold, and Mercury in the U.S.*, vol. i., p. 104.

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mass begins to melt down, until, after a half to three-quarters of an hour, the retort has received its full charge. The condenser, which is usually of sheet iron, with a small hole for the escape of vapours, is then luted on, and the temperature kept as high and as steady as possible, for any irregularity causes accumulations of crust on the lead, and of blue powder on the

Fig. 139.

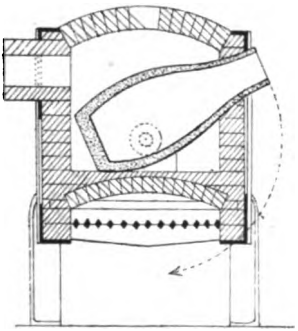
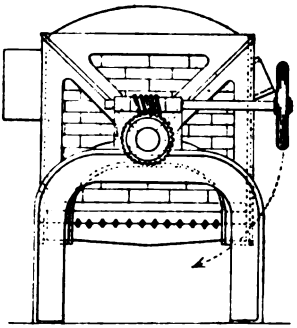
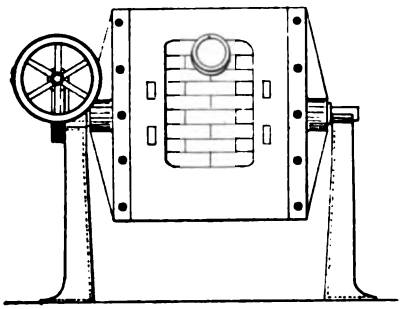


Fig. 140.





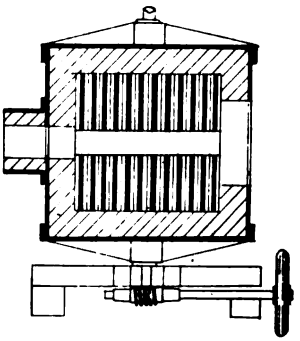


Fig. 141.

Fig. 142.

Figs. 139-142.—Faber du Faur Tilting Furnace.

neck of the condenser. The distillation takes from six to twelve hours, according to the size of the retort and the type of furnace employed, and the end is known by observing that no more zinc continues to be condensed after tapping off that in the condenser. The lead is then ladled out through the neck of the retort in furnaces belonging to classes *a*, and *c*, tapped out from the bottom in those of class *b*, or, finally, poured by tilting, in the case of the Faber du Faur furnace. In any case, after

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emptying the retort of lead, it is essential that all retort dross, charcoal, and slag adherent to the sides of the retort be carefully scraped out through the neck with an iron scraper, as also, in the case of direct heated retorts, that clinkers adherent to the outside be removed. The latter operation is much facilitated by coating the outside of the retort with a thick clay wash. A quantity of fine charcoal is then thrown into the retort to prevent formation of litharge, which would soon cut through the sides, and then another charge is added. With a good system the time lost in charging and refilling should not exceed twenty minutes.

Inclined retorts are frequently turned round in their supports in order to expose a different part of the retort to contact with the surface of the lead-bath; they are best rotated a quarter of a turn after each ten or a dozen charges.

Rösing * proposed to facilitate distillation in a tilting furnace by pouring in molten pig iron to expel the zinc. After all the zinc was condensed, the furnace was tilted, the molten iron poured off (to be used over again), and then the lead poured out as usual. The innovation, however, has not stood the test of practical convenience in working.

Examples of the Distillation Process.—At *Port Pirie* † the battery of retorting furnaces consists of twenty-four of the furnaces, shown in Fig. 138, side by side in two rows, the total capacity being sufficient to treat the crusts from 1000 tons of bullion per week, though at present only half the plant is in use. The charge for each retort is 1400 lbs., which takes three-quarters of an hour to add and melt down, about one shovelful of charcoal being mixed with it roughly. The retorting of this enormous charge takes sixteen hours, after which skimming the rich lead ("retort bullion"), ladling and scraping take about one and a-quarter hours more. The condenser is a simple sheet-iron affair placed against the front of the furnace, resting on the mouth of the retort and plastered with clay. The "retort bullion" varies in silver contents from 4000 to 5000 ozs. per ton (12½ to 15 per cent. Ag), averaging, however, 4800 ozs. The "blue powder" produced is very small in amount (from 1 to 2 per cent. only), and goes back to the smelting furnace with litharges, &c. Various other data about the operations compared with similar particulars about other works are given in the following Table XLII. :—

* *Berg- und Hüttenmännische Zeitung*, 1890, p. 369.
† *Private notes*, 1896.

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TABLE XLII.—Work Done in Zinc Distillation Furnaces.

	Baglilt.	Average, U.S.A.	Branbach.	Freiberg.	Port Pirie.	
					Silver.	Gold.
Reference, . . .	1.	2.	3.	4.	5.	6.
Type of furnace used, . .	*a*	*d*	*b*	*a*	*c*	*c*
Weight of charge, . . lbs.,	550	1000	605	500	1400	...
Time required, . . hours,	8	8	12-13	8-9	16	...
Kind of fuel, ...	coke	coke	coal	coke	coal	...
Consumption of fuel, . per cent.,	62·5	55	60-70	90	50	...
Life of retort, . . charges,	40	40	150	80	80	...
Products per 100 parts of crust—						
Rich lead, weight per cent.,	....	70-80	60	57·2	83	...
,, silver contents, . ozs.,	...	1200-3200	3500	2401	4800	1100
,, gold contents, . ,,	...	...	...	$6\frac{1}{16}$	...	...
Retort dross, weight per cent.,	15	5-8	3	5·8	8·2	35-40
,, silver contents, ozs.,	...	...	...	1503	3500	600
,, gold contents, ,,	...	...	...	$3\frac{5}{16}$	...	...
Blue powder, weight per cent.,	...	...	...	7·2	1-2	...
Condensed zinc, ,, ,,	15	10	14	29·5	7·1	...
Percentage of zinc recovered, .	45	60	60	50-90	67	...
Composition of crust treated—						
Silver, . . oz. per ton,	...	...	...	1486	4300	750
Gold, . . ,,	...	...	...	5	...	13
Percentage of zinc contents of crust recovered, . . .	...	80	96	90	...	...
Rich alloy, copper contents, %	...	...	...	...	...	5·5
,, zinc contents, . %	...	...	...	...	1·0	0·3
Retort dross, lead contents, .	...	...	...	...	74	73
,, copper contents, .	...	...	...	...	...	12

References.—1, 3, and 4. Schnabel, *Handbuch der Metallhüttenkunde*, vol. i., pp. 553-557. 2. Hofman, *Metallurgy of Lead.* 5 and 6. *Private notes.*

Comparison Between the Different Furnaces.—The suitability of one or other type of furnace depends on local circumstances. The Faber du Faur furnace requires less labour, but it is much more expensive in retorts, owing to the direct contact of the coke with the outside. Hence, where retorts are replaced with comparative ease and labour very dear, as, for example, in the United States, this furnace offers many advantages. In England and in Germany where the cheapness of labour is even more pronounced than the facility of replacing retorts, fixed furnaces are preferred everywhere but at *Mechernich.*

In Australia, economy of the expensive retorts, which can only be procured from England, is the first desideratum, and,

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accordingly, the directly-heated tilting furnace cannot compete with the flame-heated fixed furnace, in which each retort lasts double as long. The Port Pirie furnace has the additional advantage that in case a retort should break * its contents are received in a space lined with cast-iron plates, whence they can be easily collected without loss, while the recovery of the whole of the contents of a broken retort from among the mass of half-burnt coke in a tilting furnace is a very troublesome and dirty job.

Treatment of Very Rich Zinc-silver Alloys.

(From the Al-Zn Process).

4. **The Sulphuric Acid Process.**—In this the alloy is melted, granulated in water, and then treated with chamber acid in lead-lined iron pots. The zinc is dissolved out as sulphate, which, after running the solution through an asbestos filter containing scrap zinc to retain traces of silver, can be crystallised out for market. The silver and lead remain together in a semi-crystalline slime, which is run through a filter press; the cakes are moistened with a saturated solution of borax dried and melted.

5. **The Electrolytic Process.**†—The alloy is cast direct from the liquation pots in which it has been subsequently melted into moulds, 14 inches by 4 inches by $\frac{1}{4}$ inch, to form the anode plates. The cathodes are circular sheets of zinc fixed upon a horizontal spindle which revolves just above the surface of the bath. The electrolyte is a solution of $MgCl_2$ saturated with $ZnCl_2$; its specific gravity is 1·2 to 1·27. The zinc is deposited in sheets with an irregular warty surface; they contain 0·0099 to 0·0044 per cent. Fe, 0·0114 to 0·0210 per cent. Cu, 0·0341 to 0·0500 per cent. Pb, tr. to 0·002 per cent. Ag, and 99·9466 to 99·9226 per cent. Zn, which sells as c. p. zinc at a high price. The silver slime contains, on an average, 74 to 80 per cent. Ag, 10 to 12 per cent. Pb, $1\frac{1}{2}$ to 5 per cent. Cu, 0·2 to 0·5 per cent. Zn, with some As, Sb, and Fe. It is stirred in a leaden vessel with very dilute sulphuric acid to dissolve metallic oxides, and pieces of iron are then added to reduce any AgCl present. The purified slime, containing 80 to 85 per cent. Ag, and about 15 per cent. Pb, is pressed into cakes, which are dried and refined upon a cupel in charges of 2 cwts. at a time, without any addition of lead, the operation taking eight hours.

* An accident which, at Port Pirie where the retorts are worked to their utmost endurance, happens about once a week on the twelve furnaces going.

† *E. and M. J.*, Dec. 2, 1893.

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Bye-products of the Parkes Process.

Besides the bye-products obtained in **softening** and **refining**, which have been already described in Chapter xv., though the latter at all events is properly a bye-product of the Parkes process, the bye-products peculiar to the Parkes process are **retort dross** and **blue powder**, both obtained in the distillation.

Retort dross is a lead-zinc-copper alloy rich in silver and containing more or less carbon, silica (from the retort), and other impurities. It may be disposed of by adding a little at a time to the regular cupelling charge, or to the bath of lead low in silver, with which a new cupellation hearth is usually charged. Sometimes it is added to the charges of work-lead in the softening furnace, after drossing, in order that its impurities may be taken up in the skimmings. This practice is, however, objectionable, since it results in contaminating the residual metal with copper and zinc, neither of which are at all desirable additions.

At *Port Pirie* * the retort dross averages nearly as rich as the original zinc crust, say in the neighbourhood of 3000 ozs. ±. It is sweated in a cupel upon a bath of lead from the crust liquating furnaces (containing, say, 130 ozs. per ton) without, however, being allowed to scorify. The sweated dross contains only 500 ozs. Ag, and, together with that from the softening furnace, is smelted for rich silver-copper matte. The process of sweating charges of dross is repeated until the bath has absorbed silver to the extent of 2000 ozs. ± per ton, when it is concentrated together with the retort bullion. Being free from zinc this "sweat lead" is found particularly useful for working up specially zinciferous and cupriferous retort bullion, such as that from the auriferous crusts.

Blue Powder contains a good deal of zinc oxide as well as from 4 to 18 ozs. of silver per ton. At some works it is mixed with charcoal and added to the next retort charge; at others it is placed in the desilverising pot before tapping in the softened lead, and in this case it serves to saturate the lead with zinc, thus saving part of the first zincing, at the expense, however, of yielding an impure, much oxidised, and very dirty first crust. The *Omaha* Works, and perhaps some others in America, find it more convenient to ship their blue powder to European zinc-works for treatment. At *Port Pirie* it is simply sent to the smelter, with other refinery products, in order to save its silver contents, no attempt being made to utilise the zinc.

Kettle dross goes back to the softening furnace; **old retorts** to the ore blast furnace.

Costs and Losses.—It is difficult to arrive at the cost of treatment by any of the processes, since refineries have a great

* *Private notes.*

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objection to publishing such figures. According to Hofman * the average cost, including softening and refining, but exclusive of salaries and realisation charges, is from £1, 1s. to £1, 5s. per ton of base bullion; including these, the cost may be £1, 13s. to £1, 17s. 6d. per ton; while, if the loss in metals and other incidental expenses be added, the total absolute cost may amount to from £2 to £2, 10s. per ton refined. These figures, of course, refer to American works; English refineries are run much more cheaply, but it is impossible to get figures for publication.

The loss of lead is rarely as much as 0·5 per cent.; that of gold (in silver not submitted to parting) may be as much as 3 or 4 per cent. where the amount is small, say only a few dwts. per ton; but with richer bullion it rarely exceeds 1 or 2 per cent. The production of silver is almost invariably in excess of the amount paid for and determined in the base bullion by ordinary commercial assay; the excess varies from ¼ per cent. up to 1 per cent. or even more in extreme cases.

Comparison Between the Parkes and Pattinson Processes.—The Pattinson possesses over the Parkes process the advantages of less complexity, of a simpler plant, and, in the case of lead already fairly pure produced by reverberatory or hearth smelting, readily yields a pure lead of specially high quality suitable for sulphuric acid chambers without any preliminary softening or subsequent refining. It is, however, not well suited to the treatment of impure blast furnace lead rich in silver, nor to gold-bearing leads.

The advantages of the Parkes process are:—

1. Lower cost of treatment to the extent of 20 to 50 per cent.
2. Production of a market lead with only 4 to 6 dwts. of silver, instead of 9 to 15 dwts. by the Pattinson process.
3. Complete recovery of traces of gold.
4. Much purer market-lead from work-leads originally cupriferous and impure.
5. Production of a lead for cupellation with 2000 to 5000 ozs. silver per ton, as against 500 to 650 ozs. by the Pattinson process.
6. At least 50 per cent. less loss of lead and silver.

* *Op. cit.*, p. 365.

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CHAPTER XVIII.

CUPELLATION AND REFINING.

General Description.—By whatever process it is obtained, the rich lead, containing from 250 to 600 ozs. per ton (Pattinson process), or 2000 to 5000 ozs. per ton (Parkes process), has to be cupelled in order to separate its silver. The cupellation process consists essentially in melting the lead in a reverberatory furnace, and exposing it to a blast of air, whereby the lead is oxidised together with the other base metals present, forming litharge of various degrees of purity which runs off, while the silver remains on the hearth. The oxidisation takes place partly by direct contact with air, and partly by the action of molten litharge, which absorbs an excess of oxygen, and so exercises a powerful oxidising influence on the underlying lead-bath.

As in softening base bullion, the bulk of the impurities oxidise before the mass of the lead, and can be removed by skimming; the *copper*, *nickel*, and *cobalt* in a dross (*abzug*), which forms during the melting down; the *zinc*, *antimony*, *arsenic*, and *tin*, if present, in skimmings (*abstrich*), which are, in the German process, removed after the dross and before the clean litharge, though in the English process no attempt is made to separate them from the bulk of the litharge. Such portion of the *copper* as may not have been removed by drossing is only oxidised gradually by virtue of the enormous excess of litharge, for it is noteworthy that cuprous oxide is reduced by excess of lead (*Berthier*). This oxidising power of Cu_2O comes into play to a considerable extent in ordinary cupellation, for when $\frac{3}{4}$ per cent. of copper is present the operation is much accelerated, and the loss of silver reduced, as is noted by Kerl.* *Bismuth* has less affinity for oxygen than lead, and remains, therefore with the silver until almost the close of the operation, finally oxidising and colouring both hearth and litharge green; advantage is taken of this fact at Freiberg as a means of extracting and utilising traces of that metal. *Gold*, of course, accompanies the silver as it does throughout the treatment of lead ores, and, being less oxidisable, is even more perfectly concentrated.

A portion of the *silver* is oxidised and enters the litharge in that condition, but during the early part of the cupellation it is mostly reduced again by the excess of metallic lead; the first

* Quoted by Hofman, *Metallurgy of Lead*, p. 369.

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formed litharge is, therefore, much poorer than that produced towards the end of the operation. The latter probably contains silver, both as oxide and metal, according to the experiments of Wait,* who found 20 per cent. of the silver contents of a very rich bismuth litharge to be soluble in dilute acetic acid. The portion insoluble in acetic acid contained 2·7 per cent. lead as well as the remainder of the silver (2·35 per cent.), so that it is probable that the bulk of the silver in litharge exists in the condition of infinitesimal particles of a rich alloy mechanically suspended in the molten litharge. Yet another portion of the silver is volatilised together with the lead, and must be condensed in appropriate fume chambers.

Leaving out of consideration here the primitive cupellation hearths sometimes conveniently adopted in very inaccessible districts,† the cupellation process may be studied under the heads of the two prevailing types of furnace—namely, the German and the English. In the former the hearth is fixed and the roof movable; in the latter the conditions are reversed. In the **German** furnace the whole charge is added at once and opportunity is afforded for the successive and separate removal of cupriferous dross, antimonial skimmings, and poor and rich litharges; on the other hand, the final yield of silver is small in proportion to the size of the hearth.

In the **English** furnace the charging is continuous throughout the whole of the concentration, but all the impurities are removed together in litharge, which has to be re-smelted. The advantages, however, of much greater capacity for a given size of furnace and smaller cost of labour and repairs, have enabled the English furnace to almost entirely replace the German type everywhere outside of Germany itself.

With both types of furnace it is advantageous to stop the process before its conclusion, and to complete it on a separate hearth; but this is very much more readily accomplished with the English than with the German type of furnace.

GERMAN CUPELLING FURNACES.

German cupelling furnaces are characterised by having a fixed hearth, the lower portion of which forms an integral portion of the furnace masonry, while the upper, or working, hearth is composed of natural marl, or a mixture of limestone or dolomite and clay (3 or 4 to 1), to which wood ashes are sometimes added (Puertollano, Spain), well tamped in against the side walls and formed into a shallow saucer-shaped cavity. The roof is a similar shallow saucer, but inverted and usually composed of

* *Trans. A.I.M.E.*, vol. xv., p. 463.

† *v.* papers by Austin and Pfordte, *Trans. A.I.M.E.*, vol. xii., p. 41; vol. xiii., p. 185; and vol. xxi.

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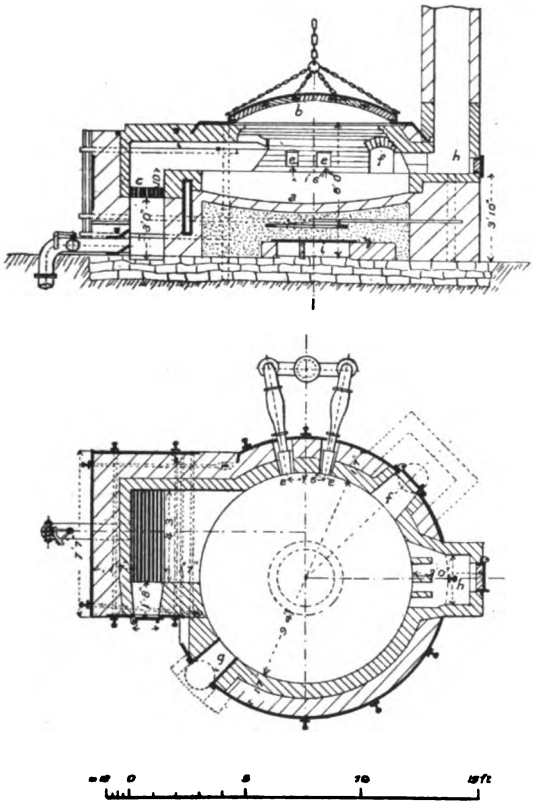
fireclay tiles made to fit the curve, joined by iron cramps or rivets and bound together by a light wrought-iron framework; ordinary firebrick is, however, often used for the roofs of small-sized hearths. The iron framework is attached to chains and can be raised and shifted by means of a crane or of a "traveller."

Two varieties of the German cupelling furnace may be mentioned—viz., the circular and the rectangular. As an example of the former (used also among other places at *Altenau*, Harz; *Hoboken*, Belgium; and *Schemnitz*, Hungary), may be described the *Lautenthal* furnace; as examples of the latter, the new *Freiberg* furnace designed by Plattner, and that used at *Przibram*.*

1. The **Lautenthal** furnace is shown in Figs. 143 and 144† in which *a* is the lower hearth of red brick, upon which the working



Figs. 143 and 144.—Lautenthal Furnace.

* Figured and described by Hofman, *op. cit.*, pp. 371, *et seq.*
† From Schnabel, *op. cit.*, vol. i., p. 584.

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hearth of natural marl containing 66 per cent. of $CaCO_3$ is tamped. The marl is first crushed and sifted, and then moistened sufficiently to ball in the hand. It must not be too wet or it will not be possible to beat it to the required degree of firmness, nor too dry or it will peel off on heating; if beaten too hard, it will crack on heating and not absorb enough litharge to prevent it from crushing; if it is too soft, on the other hand, it will absorb too much litharge. The saucer-shaped and movable roof of fire-clay tiles clamped together is shown at *b*, resting on an iron ring and hung on chains; at *c* is the grate, supplied by a gentle and easily regulated blast of air, so as to give complete combustion of the inferior slack used as fuel; it is separated from the hearth by the air-cooled firebridge. At *e e* are the tuyeres for oxidation of the lead; *f* is a working and charging door; *g* the litharge notch through which the molten litharge runs continuously; *h* is the flue leading to the fume condensing chambers; and *i*, a vault beneath the hearth to assist in keeping it cool. The workmen at the doors *f* and *g* are protected from the lead fumes by means of sheet-iron ventilating hoods, which receive their draught from the main flue.

The charge in this furnace, with its 65 square feet of area, is 10 to 12 tons of rich lead; this is worked off in thirty-six hours direct to crude silver, which is subsequently refined in crucibles.

2. The **Freiberg** furnace* is oblong in shape, though the actual hearth is elliptical inside. The roof of this furnace is flat, instead of being dome-shaped, and it is not swung on one side by a crane, but lifted by means of Weston blocks, and shifted longitudinally by means of an overhead traveller. A further peculiarity in this furnace is that the litharge notch is situated at the opposite end to the firebridge, and immediately under the flue which carries away the products of combustion as well as the lead fumes.

Mode of Working.—A new hearth must be very carefully warmed up to prevent cracking, after which the pigs of rich lead are charged in through the working doors (frequently upon a layer of straw to protect the bottom), the roof lowered into place and luted, the litharge door closed (leaving only the litharge channel or notch), the fire urged, and the blast let on gently. The lead melts down, and in doing so leaves a dross which rises to the surface of the bath and is skimmed off. Next, a lot of brown skimmings, containing arsenic and antimony, form and run off through the litharge notch, and, finally, as oxidation proceeds, nothing but clear yellow litharge is formed. The level of the litharge notch must be regulated by cutting away the rim of cooled litharge, as it forms, with an iron hook; but only sufficiently so as to leave a rim of molten litharge from 12

* For figure *v.* Schnabel, *op. cit.*, p. 588.

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inches to 20 inches wide round the edge of the lead-bath; otherwise, there is a great loss of lead and silver by volatilisation. Litharge, melting at 954° C., requires a temperature of 1000° to be kept up in the furnace, and at this temperature the lead volatilises very fast, if too much uncovered.

The blast pressure is usually about 8 ozs. per square inch, and the volume required varies from 200 to 300 cubic feet per minute, more being required the larger the furnace, and more always toward the end of the cupellation than at the beginning.

The litharge issuing from the furnace collects either in thin sheets on a cast-iron plate, when it remains yellow on cooling; or it is collected in moulds forming large masses which, when slowly cooled, acquire a red colour. Only the litharge produced about the middle of the process (about one-third of the whole), is sufficiently pure to be sold as such, the first third being too impure and the last too rich in silver. At the end of the operation thin films of litharge, driven by the blast over the surface of the silver, give rise to a play of iridescent colours; and, finally, the phenomenon of "brightening" takes place as with silver assay beads.

TABLE XLIII.—German Cupellation.*

	Freiberg.	Clausthal.	Przibram.	Müsen.
Capacity of hearth at once, . . tons,	...	10	25	25½
Total quantity worked off, . . ,,	50	10	25	25½
Value in silver, . . ozs. per ton,	650	115	170	...
Number of tuyeres to furnace, . .	2	2	3	1
Time taken for process—				
Preparing hearth and charging, hours,	...	2	18	3
Melting down, ... ,,	...	2	16	24-27
Removing drosses, . . . ,,	...		6	9
,, skimmings, . . ,,	...	4	9	144
Running market litharge, . . ,,	...	...	23	117
,, rich litharge, . . ,,	...	28	18	
Total time required, . . . ,,	178	36	80	300
Kind of fuel employed, ...	lignite	coal	coal	wood
Fuel consumption, . . . per cent.,	27	21	19·6	50
Weight of crude silver obtained, . lbs.,	...	37½	...	154
Percentage weight of dross and skimmings,	...	5	...	28
,, ,, foul litharge, . .	76	86	...	52
,, ,, market ,, . .	12½	...	36	30
Assay of market litharge, ozs., dwts.,	...	1 12	1 6	1 12
Percentage loss of silver, . . .	...	...	0·83	...
,, ,, lead, ...	...	...	4·33	...

* This information is mostly condensed from Schnabel, *op. cit.*, pp. 595-598.

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After the brightening, two pieces of flat bar iron are stuck into the cake to serve as handles, and the hearth is cooled by water from a hose. The cake is then removed, and the hearth, after cooling, is broken up with a pick, screened, and re-tamped, only those portions which are saturated with litharge going to the blast furnace. The silver cake, still containing from 2 to 10 per cent. of lead and other impurities, may be refined on another small cupelling hearth, or in crucibles, as subsequently described.

The time required, consumption of fuel, losses of lead and silver, &c., are for several leading German works given in Table XLIII.

Variations in the Method.—The above is the ordinary method of cupellation in the German hearth, but sometimes the rich lead is only cupelled down to from 50 to 80 per cent. silver in the large cupelling furnace, and is then tapped into moulds, the cupellation being finished on a smaller hearth, where also the silver is refined. In this case it is usual to add more lead in the large furnace as the first charge oxidises away, somewhat as in the English furnace, the total quantity treated at once thus frequently amounting to twice or thrice the weight charged at the beginning.

This practice is adopted at Freiberg, where, as already mentioned, the rich lead concentrated by the Pattinson process contains a notable percentage of bismuth. The rich lead, in quantities of 50 to 60 tons at a time, is concentrated up to 80 per cent. silver in the large furnace already described (which takes seven and a-half days), and then the concentrated alloy is cupelled in a smaller hearth to silver, which, after refining on the same hearth, is 998 fine; a bismuth litharge with 4 to 8 per cent. Bi is here formed, also a green bismuth hearth under the cake of silver, which contains 6 per cent. Bi; these are treated for the manufacture of bismuth salts by solution in hydrochloric acid and precipitation of bismuth oxychloride by dilution with water.

The same system of concentration is in use at Schemnitz,* where 20 to 30 tons are charged gradually into a hearth holding only 8 tons.

Absorption.—The German cupelling furnace is much more frequently employed than the English for the operation of "absorption" (*eintränken*), in which rich argentiferous ores or residues are fed gradually into the bath of molten lead, which absorbs the greater part of their silver contents, while the other metals become oxidised, and, together with the siliceous earthy constituents, are more or less completely fluxed and carried away by the litharge or raked off the surface of the bath. This practice is common at *Altenau* and *St. Andreasberg* (Harz), where silver ores containing upwards of 2000 ozs. silver per ton are

* Schnabel, *op. cit.*, p. 598.

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habitually treated by this process, as much as 5 per cent. of the weight of the lead being added. It is also in use at *Hoboken* (Antwerp), and *Lautenthal*, where retort dross, oxidised zinc crusts, and other residues are fed in the proportion even of 60 to 100 per cent. of the rich lead operated upon with satisfactory results, though the duration of the process is somewhat lengthened.

The use of a lead-bath on a cupellation hearth for extracting the silver from sulphide precipitates obtained by lixiviation will be described in Part ii., Chapter xiii.

Refining.—The crude silver obtained in the German furnace has always to be refined on a separate hearth owing to the traces of lead, copper, nickel, bismuth, &c., which it obstinately retains. The refining may be conducted on the hearth of a small cupelling furnace as at *Freiberg* and *Przibram*, or in crucibles, as at *Lautenthal*, *Frankfort-am-Main*, and *Hoboken*. The former method calls for no description here, as the manipulations are identical with those in the English method shortly to be described.

Use of Silver Sulphate.—Rössler found * that silver sulphate added to molten crude silver rapidly oxidised first the lead and then the bismuth, having, however, little or no effect upon the copper. The crude silver at Lautenthal and Hoboken contains bismuth, but very little copper, so that this method is well suited to its refining. The crucibles employed are of plumbago, hold about 700 lbs. of the crude silver (950 to 980 fine), and are heated in a wind furnace supplied with air by two blast pipes just above the grate bars. In order to protect the crucible from corrosion by the slag, a section of wrought-iron pipe, 2 or 3 inches smaller in diameter than the crucible, and 7 inches long, is coated on both sides with clay, heated, and then placed on the molten bath, into which it sinks several inches. Into the centre is placed 8 or 10 lbs. of silver sulphate in lumps of egg size (prepared by dissolving silver in sulphuric acid, evaporating to dryness, fusing, and casting in moulds), and previously warmed. The silver at once begins to boil and the sulphate melts, forming a layer on the top, which has to be stirred in with an iron rod until there is no further action. The slag is then stiffened with sand or pulverised quartz and removed with a skimmer, when another addition of sulphate is made. The total quantity required is found in practice to be twice the weight of base metal removed; thus 700 lbs. of silver (970 fine and containing 21 lbs. of base metal) require about 40 lbs. of silver sulphate, which is added 8 to 10 lbs. at a time. The test for fineness is to dissolve a portion in nitric acid and add excess of ammonia, when any turbidity (bismuth) shows that a further addition of sulphate is required. Part of the silver remains in the slag,

* *Berg- und Hüttenm. Zeitung*, 1889, p. 387.

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which contains * SiO_2 40·7, PbO 33·50, FeO 13·47, Bi_2O_3 6·01, Ag_2O 2·05, and traces of Cu, P, CaO, &c.

The great advantage of this method of refining lies in the fact that the bismuth is wholly concentrated in the last slags, the first being practically free from that metal, and the small quantity of rich slag thus produced is easier to work up for bismuth than the litharge and cupel bottoms obtained in reverberatory refining. The loss of silver is also said to be smaller than in refining on the cupel, presumably on account of the smaller surface exposed, and of the fact that it is covered with slag during the operation. The cost, both for labour and material, is, on the other hand, much greater.

ENGLISH CUPELLING FURNACES.

These are characterised by their comparatively small size, by the possession of fixed roofs and movable hearths, and by the fact that the rich lead is always charged continuously, so that the final cake of silver produced is very large in proportion to the size of the furnace.

The roof must be as low and as flat as possible, and the grate area large, as a very high temperature is required to keep such a large mass of silver in a molten condition towards the end of the process, and more particularly for refining when this is done in the same "test," as was formerly the invariable practice. The more modern practice, however, is to concentrate up to 60 or 70 per cent. silver in one furnace, and then finish the cupellation and refine in another. The hearth (called a "test") may be either oval or rectangular, but the latter form is peculiar to American works.

Fig. 145 is a front elevation of an English cupelling furnace of common type, Figs. 146 and 147 † being sections of an American furnace of somewhat similar construction. In the latter *a* is the fireplace, *b* the flue, *c* the vault between the firebridge, *d*, and the flue-wall, *e*, into which the test carriage runs; *f* is the iron compass ring, *h* the ashpit, *i* and *j* are cast-iron plates to support the bridge and flue-walls respectively; *k* is the charging door-frame with its sliding door, *o*, and *l* is the litharge door. Some furnaces have three doors at the back, but in that here figured the lead is fed, one pig at a time, through the same door in which the tuyere is inserted. The whole upper part of the furnace, as well as the front and flue are enclosed in cast-iron plates (Fig. 145), and well bound with buckstays and tie-rods (not shown). The flue exit is divided into five small flues gradually increasing in size towards the front, so as to spread the heat in that direction where the cooling effect is greatest.

* *v.* complete analysis, *E. and M. J.*, Nov. 14th, 1891.
† Hofman, *op. cit.*, p. 381.

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In this furnace the compass ring is square with rounded corners (Fig. 147), the hearth having, of course, the same form and fitting tightly inside it with the help of a clay lute. It is open in front for 16 inches, in the centre of which space comes the litharge notch 4 inches wide.

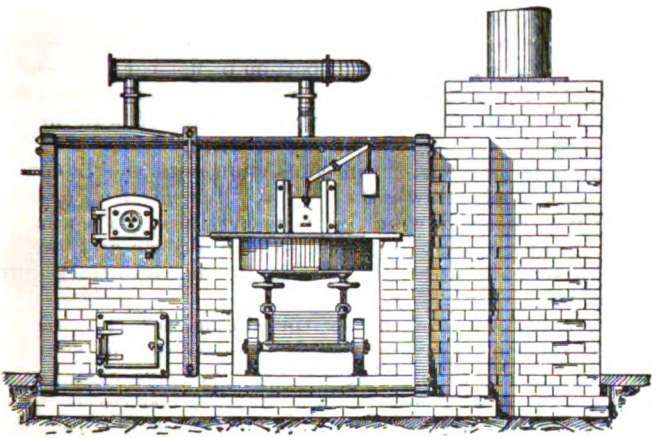
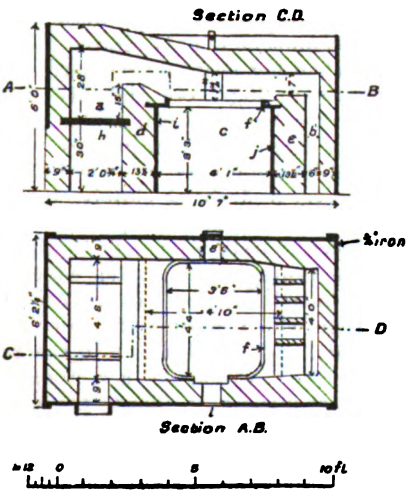


Fig. 145.—English Cupelling Furnace.



Figs. 146 and 147.—American Cupelling Furnace.

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The tuyere (not shown) is a 3-inch sheet-iron pipe, which is either flattened at the end so as to deliver a sheet of air 4 inches wide by ½ inch thick, or else fits into a cast-iron nozzle of that shape. The blast may be produced by either a fan or a positive blower, and the average pressure, according to Hofman,* is not more than 4 ozs. per square inch. At *Port Pirie*, with a flat nozzle of the same size, a pressure of 10 or 12 ozs. per square inch is used, which is usually, however, partially shut off.

Test Rings and Supports.—The common style of test ring is a simple oval with a skeleton bottom of flat bars, all made of cast iron in one piece, and into which the hearth material is rammed. The pattern shown in Figs. 152 and 153 is an improvement on this for concentration work, since, besides the lip or spout in front for pouring (in connection with the Lynch test support described below), the ordinary upright rim, *b*, is cast with a 3-inch flange, *a*, which, with its clay lute, fits against the bottom of the compass ring and so makes a closer joint. In both of these tests the hearth material is tamped to the required shape by the eye only.

In the oldest style of furnace the simple test ring was supported merely on transverse bars inserted across the vault, and levelled up by means of wedges. This primitive arrangement, however, gave place many years ago to the test carriage, with four adjustable jack-screws, shown in position in Fig. 145, and a somewhat different form of which is again shown in Figs. 148 and 149.

This form of test carriage has come into very general use, and is extremely convenient, except where pouring from the test is practised, for which it possesses the disadvantage that the position of the test cannot be readily altered during cupellation, as the jack-screws when hot become very hard to turn.

The furnace shown in Figs. 146 and 147 with rectangular compass ring has, of course, a rectangular test, one form of which, with tilting carriage, is shown in Figs. 150 and 151.†

This test ring, unlike the others, has a solid cast-iron bottom, *a*, upon which is a layer of firebrick closely laid. The cast-iron pattern, *b*, shown in the figures in place, is then oiled and inserted, and the hearth mixture (cement in this case) rammed tightly into the intervening space; after which the pattern is withdrawn and the hearth dried as usual. At *c* is the aperture for the litharge notch, which consists of a slot in the front of the casting, 3 inches wide, which is filled up to the required height with the mixture. The advantage of a rectangular test is that, for any given width of furnace, it affords the maximum of surface, and, therefore, the maximum of oxidising effect; oval tests, however, generally stand better.

* *Op. cit.*, p. 389. † Adapted from Hofman, *op. cit.*, p. 383.

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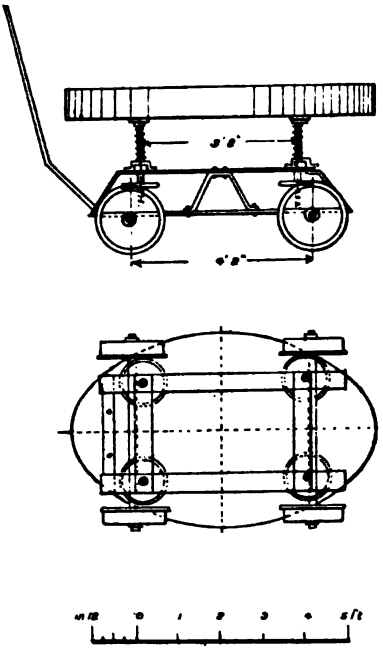
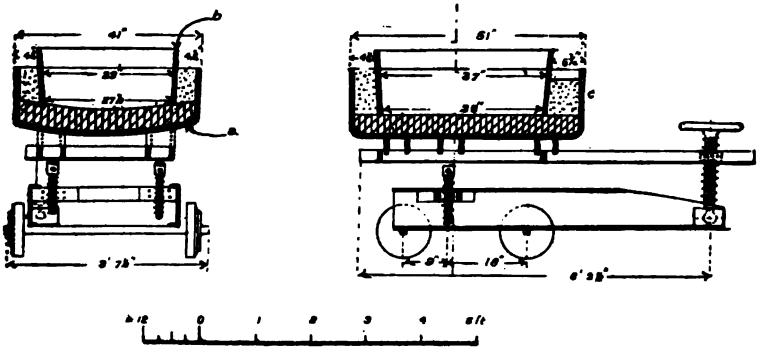


Figs. 148 and 149.—Test Carriage.



Figs. 150 and 151.—Test Carriage.

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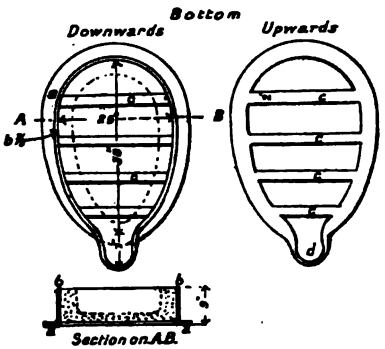
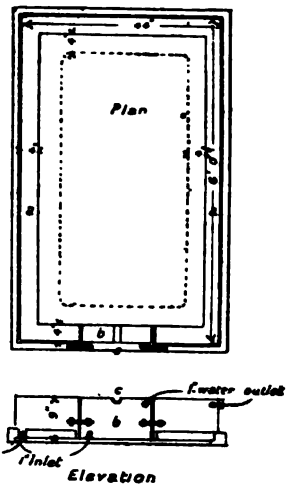
The test carriage shown with this brick-bottomed test is peculiar in being provided with a simple hand-wheel arrangement at one side of the front for lowering the front of the test ring as the cupellation proceeds, so as to regulate the flow of litharge without cutting down the litharge notch, and also to permit of pouring the contents of the test if required.

With all the above test rings the litharge very soon eats away the material forming the test, and, therefore, many devices have been adopted for cooling by means of water pipes coiled round the test ring, &c., combined often with a separate water breast, so as to diminish the corrosion. One of these devices in common use in America is the completely water-jacketed test of Steitz, shown in Figs. 155 and 156. The water jacket, *a*, of boiler iron is rectangular and complete, except in front, where a smaller cast-iron jacket, *b*, bearing the litharge notch, *c*, is bolted on. The only wear of the jacket is in this notch, and when it is worn through, the small breast jacket is taken out and replaced by a new one. This form of test ring for concentrating rich lead up



Figs. 152 to 154.—Test Rings.



Figs. 155 and 156.—Water-jacketed Test.

to 70 per cent. silver has the advantages of trebling the life of the hearth material, while saving trouble with the litharge notch, which remains at a constant level and suffers no corrosion. This constant level of the notch, however, coupled with the enormous cooling effect, renders it impossible to bring up the enriched alloy to fine silver on such a test; consequently, the Steitz test is used for concentrating alone.

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Not only, however, is the cooling effect with these completely water-jacketed tests so great that more fuel has to be employed to avoid retardation of the process, but the tests themselves are greatly racked by the varying degrees of intense heat to which they are subjected, and soon begin to leak at the seams. For these reasons metallurgists outside of the United States generally prefer the plain oval flanged cast-iron test ring, with a 1-inch pipe all round, fitting tightly against the ring and imbedded in the material of the test. At the front is a small cast-iron tapping breast carrying the litharge notch or lip. The breast is easily replaceable when it begins to leak, though it usually lasts out from five to six tests. Before using one of these breasts over again it is tested for leaks by hydraulic pressure in order to minimise the danger of springing a leak while the cupel is running.

When the system of concentrating and finishing on a separate hearth is adopted it is convenient to be able to tilt the test so as to pour the molten alloy into moulds. This can be done with the hand-wheel carriage shown in Fig. 151; but the Lynch test support, shown in Fig. 157,* is also very convenient. It consists

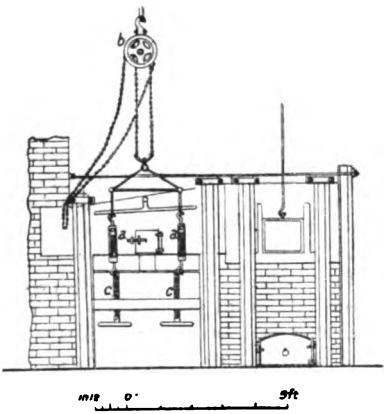

Fig. 157.—Lynch Test Support.

of two bars on the lower side of the test ring, by means of which the front end of the test is supported upon two turnbuckles, *a*, which in turn, by means of an iron triangle, hang from a differential chainblock, *b*. The back of the test rests upon jack-screws, *c*, working in a fixed bar. With the block the front of the test can be easily raised or lowered during cupellation as required, and, with the turnbuckles, either side can be raised or lowered so as to regulate the corrosion of the hearth.

* Blake, *Trans. A.I.M.E.*, vol. x., p. 220.

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This support is never required for water-jacketed tests with a constant discharge level, which are, therefore, commonly mounted on one or other of the forms of carriage already figured; whereas the Lynch support is sometimes seen in America on finishing tests which are not water-jacketed, and when it is thought more convenient to pour the silver than to ladle it. The total quantity to be handled, however, on the finishing test is so small that, even in the United States, it is more common to use the fixed jack-screw test carriage and ladle out the fused silver into moulds, instead of attempting to pour it.

Hearth Material.—Formerly the only material used for the tests of English furnaces was **bone-ash**, which is still commonly used in England itself for that purpose. At *Eureka*, Nev., bone-ash has been practically superseded by mixtures of **siliceous limestone** and **clay** (in proportions of from 2 to 5 per cent. of the former to 1 of the latter), ground to pass a 12-mesh, and **Portland cement**, which has given excellent results at many American works; a mixture of cement and ground **firebrick** has also given good results.

Bone-ash must not be beaten down too hard, as that would make the test crack on firing. The limestone-clay tests, however (and, according to Hofman,* those of cement also), must be tamped as hard as possible, and dried, and warmed very gradually and thoroughly. In using cement it is essential to do the tamping as *rapidly* as possible before it commences to set.

The bottom of the test shown in Figs. 150 and 151 is made of firebrick, and experiments have been made with **magnesia brick** as a lining for sides as well as bottom,† but no results have been published. A brick hearth is specially used for refining argentiferous matte into bottoms (*v.* Chapter xvii.).

Whatever its material, the hearth should be dried out for at least a month before commencing to warm up. A plain (not water-cooled) cement test used right through for concentrating as well as finishing may last seven days, while one used four or five hours daily for finishing only will last for months, and even a limestone-clay test, under these circumstances, lasts a month; a water-jacketed concentrating test of limestone-clay will last two months.‡

At *Port Pirie*,§ all the tests are alike, except that those used for finishing have no water-cooled lip or litharge breast. The mixture employed is fireclay, siliceous limestone, and Portland cement in certain proportions, which are mixed dry, damped to the required consistency, and quickly *pressed* into the test, which lies bottom upwards upon a cast-iron mould the shape of the required cavity Contrary to what is stated by Hofman,

* *E. and M. J.*, Mav 4, 1893. † Hofman, *Metallurgy of Lead*, p. 391.
‡ All these figures are on the authority of Hofman, *op. cit.*, p 392.
§ *Private notes.*

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it is found that beating down a cement test too hard injures its durability. The gentle ramming is done as quickly as possible before the cement commences to set, just sufficient pressure being exercised to get out all the air in the interstices, and then the test is immediately turned up and filled with water, which is allowed to be absorbed and to evaporate naturally. The tests are then piled in a warm part of the refinery, where they dry out as gradually as possible during four to six months before being used. The average life of tests prepared in this way is, for concentrating up to 50 per cent. concentrated bullion, three weeks, at an average of 30 bars per shift, or, say, a total of 72 tons lead passing through the test, at the end of which its capacity has become enlarged from 1 to 2 tons. On the finishing side of the cupellation house each test lasts, on an average, ten days, going constantly day and night, or while an average of 400,000 ozs. silver is cupelled upon it.

Mode of Working.—After gradually heating up the test to a red heat, lead is charged through the front and back openings, and, when melted down so as to fill the cavity, the blast is turned on and cupellation started. The litharge runs off at the litharge notch, and the rate of running off is regulated, partly by the rate at which pigs of lead are fed forward at the tuyere door, partly (in tests unprovided with water breasts) by the depth of the litharge notch. In any case, it is usual to keep about half the lead covered with litharge to reduce the loss by volatilisation. When the test has become filled with rich alloy (sometimes called "**bullion concentrates**"), the blast is stopped, the contents of the test removed into moulds by ladling or pouring, and a new concentration begun, the furnace working continuously as long as the test lasts.

The operation of "**finishing**" is conducted similarly, but at a higher temperature, in an uncooled test, until sufficient crude silver is obtained, when the addition of pigs of concentrated alloy is stopped, and the last litharge removed. The phenomenon of "brightening" is seldom or never seen on the English hearth.

Refining of the crude molten silver is sometimes conducted in a separate hearth, but generally in the finishing hearth itself, and by the blast alone. A little bone-ash, however, is sprinkled on to absorb base metal oxides, and, generally, also a few shovelfuls of soda nitre, one at a time; the slag so produced is usually not removed until just before casting. The refining is concluded when the metal has a clean, smooth, brilliant surface, like a mirror, which does not become tarnished on stirring, and when a small sample bar shows a finely granular silky fracture and great malleability. It is usual, however, to make careful assays before casting, in order to be sure that the bars will be above the standard for fine silver (viz., 997 +).

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Casting is occasionally done with the help of the Lynch test support already described, the silver being poured direct into the moulds, but more usually the metal is ladled out into the warmed moulds. The sample is best taken from each mould as poured, and just before "setting," by means of a long iron spoon.

Examples of English Cupellation.—At *Eureka* (Nev.)* bone-ash tests, holding 1 ton each, are filled with rich lead, containing 550 ozs. silver, which is melted down and fresh lead added as fast as it oxidises. Once in each twenty-four hours the rich alloy is tapped, yielding six to eight bars of 60 to 70 per cent. silver. In the "finishing" operation sixty such bars are cupelled in sixteen hours, giving 16,000 ozs. of doré silver, 965 fine in silver, and 30 in gold. From the concentration some litharge is obtained, running only 1 oz. Ag per ton, which is reduced to market lead in a reverberatory with charcoal. The litharge from the finishing test all averages 75 ozs. per ton, and goes to the ore furnace.

At *Port Pirie* (S.A.) there are six concentrating hearths and two finishing hearths, all being alike in general form and dimensions. In the former, the bars of rich bullion ("retort bullion"), averaging 4500 ozs. Ag per ton, are melted down with a 12-oz. blast at the rate of thirty bars (say, 22 cwts.) per 8-hour shift, the capacity of the hearth being from 1 to 2 tons, according to the amount of corrosion it has undergone. Concentration is stopped when the lead reaches 15,000 to 16,000 ozs. to the ton, and the contents of the test are then ladled out into moulds. The litharge from the concentration averages only 30 ozs. per ton, and is smelted in the refinery blast furnace together with siliceous ores.

About ½ ton of the bars of concentrated bullion are melted down in the finishing hearth, and cupellation is begun, more being added at the back, as usual, to supply the place of that oxidised. The rate of cupellation on these finishing tests is about 14,000 ozs. of silver per 8-hour shift, and the quantity of silver produced from one filling is about 23,000 ozs., which is ladled out by hand into moulds, sprouting and effervescing violently as it solidifies. The average fineness of the finished silver is about 997½, the chief impurity present being copper, which obstinately remains after all the lead has been removed. The litharge produced on the finishing hearth contains about 200 ozs. Ag per ton, and goes to the softening furnaces to assist in the oxidation of antimony, as explained in Chapter xv.

The silver is "dried," or refined, upon a perfectly new finishing test by exposure for six hours to the action of the blast, which oxidises the last traces of base metals. No fluxes are employed, but a little bone-ash or hearth mixture is sprinkled on to the bath towards the end of the operation in order to collect the

* Curtis, *Mon. U.S. Geol. Survey*, vol. vii., 1884.

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floating oxides in a stiff slag, which is then removed by touching with an iron rod, to which it adheres. After careful skimming the silver is cast into bars, which assay from 998·5 to 999·4 fine.

This silver was found to be too fine for the market, and accordingly of late the ingots have been re-melted in large plumbago crucibles in a wind furnace with the addition of a sufficient proportion of copper to reduce the fineness to 997 exactly. The melting is done without fluxes, and any small quantity of slag formed is removed by touching it with a cold iron rod immediately before pouring. The moulds are perfectly clean, warmed, and blackleaded, but no oil or other substance is found necessary to give a clean surface or prevent sprouting. Just before pouring, a single large stick of charcoal is laid across the surface of the metal, and this is found to absolutely prevent all sprouting during cooling, provided the metal is poured at the right temperature—*i.e.*, not too hot. Sometimes a little slag is found on the top of the bar, but this is so small in amount that one man can clean, chip, weigh, and stamp sixty bars in a day of eight hours.

Losses by Volatilisation.—There are very few figures obtainable on this point. The average loss of lead, however, on the whole refining process is supposed to vary between 3 and 8 per cent, by far the largest part of which is in the cupellation; similarly, the true loss of silver varies between ½ and 1½ per cent., mostly in the final stages. Even of these amounts, however, a portion is always recovered from the fume chambers. At *Kongsberg*,* the loss of lead is said to have averaged formerly 6½ per cent. of all the lead melted on the cupel. At *Przibram*,† the cupellation losses average 0·83 per cent. of the silver, and 4·33 per cent. of the lead.

Owing, however, to the use of the ordinary *uncorrected* low temperature cupellation—or combined scorification and cupellation—assay for the work-lead or base bullion treated, the working loss of silver is usually well within the assay loss, and, consequently, most refineries are able to show an apparent excess of production, or *plus* clean-up, which may reach as much as ½ per cent. on the total silver turned out.

Comparison between the German and English Methods.—The advantages of the German system of cupellation in connection with comparatively low grade rich leads, such as those from the Pattinson process, are:—

1. Smaller consumption of fuel.
2. Possibility of producing a considerable proportion of pure market litharge free from impurities and low in silver, which sometimes sells better than lead itself.

* Percy, *Metallurgy of Silver and Gold*, vol. i., p. 512.
† Schnabel, *op. cit.*, vol. i., p. 597.

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The English system is specially suited to the treatment of the rich lead obtained by the Parkes process, but it possesses the following general advantages:—

1. Smaller first cost of plant for a given output of silver.
2. Saving of 50 per cent. or more of the labour cost.
3. Saving of three-fourths the cost of hearths and hearth material.
4. Smaller quantity of hearth material to be re-smelted.

Except in Germany itself, the German type of furnace has been almost entirely superseded by the English furnace with its modern improvements.

Analyses of Cupellation Products.—The following table shows the composition of products of cupellation, chiefly at Przibram:—

TABLE XLIV.

	Przibram.				Litharge.
	Antimony Skimmings.	Litharge.	Cupel Bottom.	Flue-dust.	
Reference, .	1.	2.	3.	4.	5.
PbO, . .	89·82	98·370	68·860	64·41	85·34
CuO, . .	0·28	0·069	0·070	...	0·61
Bi_2O_3, .	...	...	tr.	tr.	0·23
MoO_4, .	...	...	tr.	...	...
As_2O_5, .	0·92	0·010	...	tr.	...
Sb_2O_5, .	5·85	0·074	0·530	11·40	0·08
SnO_2, . .	tr.	...	...	...	...
Ag, . .	0·004	...	...	...	2·94
Ag_2O, . .	...	0·004	0·070	0·013	...
Al_2O_3, .	0·32	0·072	2·120	...	...
Fe_2O_3, .	0·14	0·010	0·300	...	0·99
ZnO, . .	tr.	0·009	tr.	0·50	0·22
NiO, . .	0·04	0·005	...	...	0·01
CaO, . .	0·95	0·256	13·50	tr.	0·26
MgO, . .	...	...	...	...	0·03
CO_2, . .	...	0·383	10·60	...	1·25
SiO_2, . .	0·37	0·320	2·97	4·35	0·12
SO_3, . .	0·22	0·034	0·04	16·65	0·32
H_2O, . .	...	...	...	...	0·24
	...	99·616	...	...	...

References.—1, 2, 3, and 4. Hofman, *Metallurgy of Lead*, p. 376. 5. Wait, *Trans. A.I.M.E.*, vol. xv., p. 463.

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Treatment of Bye-products.—The bye-products of cupellation (leaving out of consideration special products containing bismuth, the treatment of which has been already referred to) are **flue-dust, cupel bottoms,** and **litharge.** The two former always go back to the ore blast furnace.

From the German hearths, treating lead of only moderate richness, part of the **litharge** is always pure and sufficiently low in silver to be sold as such, the remainder is smelted to lead, either alone or in the ore furnace. The litharge from the English furnace treating enriched lead is never poor enough in silver for market, and must be smelted, either with dry silver ores or alone, though sometimes a portion of it can be advantageously added to impure leads in the softening furnace, as already seen.

At *Schemnitz* (Hungary), *Sala* (Sweden), and perhaps some other places, the stream of molten litharge from the furnace runs direct into small iron cylinders filled with glowing charcoal standing on a grate over an iron pot. The litharge is completely reduced to metal by the glowing charcoal, the consumption of which does not exceed 10 per cent. by weight of the lead produced.* Any fume given off is drawn into the main flues by means of a hood.

* Theory requires less than 6 per cent.

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APPENDIX.

THE remarks on p. 272, with reference to the Wetherill process of Magnetic Separation, were originally penned some two years ago, since when the author understands that experiments with this process on a working scale have been undertaken by some of the Broken Hill Companies, with a view to testing its applicability to the conditions there prevailing. No particulars have, however, to the author's knowledge, been hitherto published as to the practical success of these experiments.

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ERRATA.

Page 13, 4th line from top, *for* "¼ grain" *read* "¼ gramme."

„ 16, 5th line from bottom, *for* "largely" *read* "lazily."

„ 28, 6th line from bottom, to second member of equation *add* "+ 2 CO."

„ 35, 9th line from bottom, *for* "hyposulphate" *read* "hyposulphite."

„ 41, 11th line, *for* "react upon the sulphide" *read* "react upon the sulphate."

„ 49, 12th line, *for* "analyses of produce" *read* "analyses of products."

„ 55, 2nd line from bottom, *for* "cut in" *read* "culm."

„ 58, Table X., 2nd column, *for* "Engir" *read* "Engis."

„ 73, Table XI., 1st column, *for* "HgO" *read* "H_2O."

„ 77, 8th line, *for* "Pearse" *read* "Pearce."

„ 81, 34th line, *for* "below" *read* "on next page."

„ 82, description, Figs. 32 and 33, *for* "Wellner stall" *read* "Improved roasting stalls."

„ 92, 9th line from bottom, *for* "rabble" *read* "rubble"

„ 97, Table XIII., 3rd column, 2nd line from bottom, *for* "20/6" *read* "2/6."

„ 110, 32nd line, *for* "Schetel" *read* "Schertel."

„ 120, 9th line from bottom, *for* "strong" *read* "stony."

„ 150, description, Figs. 65 and 66, *for* "arrangements for charging furnaces" *read* "Broken Hill Block 14 furnaces, Port Adelaide, S.A."

„ 152, 27th and 28th lines, *for* "T-beams" *read* "I-beams."

„ 152, 2nd line from bottom, *for* "brick stays" *read* "buck-stays."

„ 156, description, Fig. 69, *for* "cast-iron" *read* "wrought-iron."

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Page 162, description, Fig. 74, *for* "Tuyere" *read* "Tuyere-box and valve."

„ 163, 27th line, *for* "trickling" *read* "buckling."

„ 166, description, Figs. 82-84, *for* "slag-pot" *read* "catch-pot."

„ 169, description, Fig. 89, *for* "large slag-pot (double)" *read* "large crane-handled settling-pots."

„ 197, footnote, *for* "Oct., 1887" *read* "vol. vi., p. 29."

„ 204, 1st line, *for* "table" *read* "rabble."

„ 238, Table XXXI., 7th column, *for* "57·31 per cent. PbS" *read* "57·31 per cent. $PbSiO_4$."

„ 307, 15th line, *for* "-pot" *read* "-pit."

„ 313, Table XXXVIII., 14th line, *for* "pans" *read* "pots."

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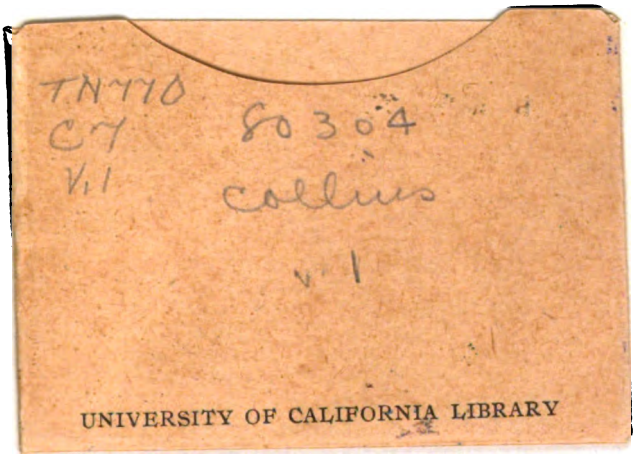

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